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## Technical Report for the Period

1. 1. 1964 to 30. 6. 1964

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EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL REPORT  
FOR THE PERIOD  
1.1.1964 to 30.6.1964

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Approved by *L.J. Bellamy*

L.J. BELLAMY  
DIRECTOR

24th August, 1964

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INGREDIENTS OF PROPELLANTS AND EXPLOSIVES1.1 PREPARATION; PROPERTIES; REACTIONSMiscellaneous Preparations

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Mononitro- and dinitrophloroglucinol have been prepared by the direct nitration of phloroglucinol for experiments on the general properties of these compounds and their salts.

Anti-oxidants

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When 3,6-bis(4-methoxyphenyl)-2,5-dihydroxybenzoquinone was heated with methanol and liquid ammonia in a sealed tube at 140°C, the expected 3,6-bis(4-aminophenyl)-2,5-dihydroxybenzoquinone was not obtained, although a reaction involving introduction of nitrogen into the molecule occurred. Elemental analysis and I.R. spectra indicated that the same product was obtained by similar treatment of the corresponding 2,5-dichlorobenzoquinone, and it may therefore be either 3,6-bis(4-methoxyphenyl)-2,5-diaminobenzoquinone or the tautomeric 2,5-dihydroxybenzoquinimine.

4-Dimethylaminoaniline was purified, and then coupled, via the diazonium acetate, with 2,5-dichlorobenzoquinone to give 3,6-bis(4-dimethylaminophenyl)-2,5-dichlorobenzoquinone, which was then hydrolyzed to the corresponding 2,5-dihydroxybenzoquinone. 4-Acetamidoaniline was similarly coupled to give 3,6-bis(4-acetamidophenyl)-2,5-dichlorobenzoquinone. Some success was achieved in hydrolyzing this to 3,6-bis(4-aminophenyl)-2,5-dihydroxybenzoquinone, and the crude product contained an effective anti-oxidant.

Impure hentriacontene-1, prepared by the destructive distillation of myricyl stearate, was purified by chromatography on silica gel/silver nitrate substrate; the high iodine number and imprecise melting point suggest that further purification should be possible.

2-Phenylquinhydrone, prepared by alkaline rearrangement of 4-phenylquinol, was successfully reduced to 2-phenylhydroquinone. The 4-phenylquinol had been prepared by the reduction of 4-nitrobiphenyl to the hydroxylamine, followed by rearrangement and oxidation. 4-Nitro-4'-tertiarybutylbiphenyl, a new compound, was prepared by nitration of 4-butylbiphenyl, this latter being obtained by Friedel-Crafts reaction between butyl chloride and biphenyl. The identity of the nitrocompound was checked by its alternative synthesis by Friedel-Crafts butylation of 4-nitrobiphenyl, and by a Bachmann-Hey coupling of 4-butylaniline with nitrobenzene. 4-Nitro-4'-butylbiphenyl could be reduced to a very unstable hydroxylamine, but attempts to rearrange this to 4-(4'-butylphenyl)quinol were not successful.

A Gomberg coupling of benzene diazonium chloride with an alkaline solution of 4-nitrosophenol gave a complex mixture from which 2-phenyl-4-nitrosophenol could be isolated; using pure nitrosophenol the yield was 12 per cent, some 3 per cent higher than previously reported. 2-Phenyl-4-nitrosophenol was reduced with tin and hydrochloric acid to 2-phenyl-4-aminophenol, which possesses interesting antioxidant properties. The amphoteric nature of this compound made its isolation difficult, and purified yields

/were .....



were low; other methods of reduction were investigated, and yields of 75 per cent were obtained by using alkaline sodium hydrosulphite.

2-Phenyl-4-aminophenol was oxidized in fair yield by acid dichromate solution to 2-phenylbenzoquinone, and this was reduced to 2-phenylhydroquinone, which was identical with that prepared above. Attempts to oxidize 2-phenyl-4-nitrosophenol directly to the benzoquinone via the tautomeric 2-phenylquinoxime were not successful.

Hydrazine Perchlorates

RESTRICTED

It has been found that all the hydrazine perchlorates are soluble in acetonitrile, as are barium perchlorate, sodium perchlorate, hydrazine, and sulphuric acid. It thus appears that much of the chemistry of these compounds can be duplicated in this solvent. All the hydrazine perchlorates are relatively stable in the boiling acetonitrile, although the anhydrous diperchlorate, which is extremely soluble, reacts on prolonged boiling, and could no doubt be dangerous if held for a long time. Seventy per cent perchloric acid and acetonitrile left overnight on the steam bath gave a crystalline residue not yet identified.

A Weighing Device for Continuously Following the Loss of Weight Inside a Vacuum

A device has been made in which a pan containing moist material is supported by a structure floating on mercury, and having a pointer which can be read by a microscope. The loss of weight of a hundred grams of material being dried in vacuo can be followed to the nearest tenth of a gram.

Results on the drying of hydrazine diperchlorate have so far shown no sharp breaks, suggesting that drying is not uniform throughout the mass of material.

Trinitrotoluene

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A series of experiments was carried out in which heated TNT was subjected to centrifuging, attempts being made to maintain the temperature by preheating the centrifuge. The results of two successful experiments are tabulated below.

TABLE 1

Set Point of TNT Used	Final Temperature °C	% Removed in Liquid State	Set Point of Products	
			Solid	Exudate
80.0°C	73.5	9.6	80.6	70.5
80.0°C	71	6.8	80.55	67.2

/As .....



As the setting point of pure TNT is  $81.0^{\circ} \pm 0.1$ , this sweating procedure effects considerable purification. The setting point of TNT is reduced by  $0.51^{\circ}$  for each mole per cent of impurity, so the final product is about 99.2 per cent pure.

When run on a thin layer chromatogram, the exudate showed two spots, which indicated impurities in grade 1 TNT to have been enhanced corresponding to their enhanced concentration. One of these spots runs close behind the main TNT front, the other is slow moving; they occurred with a number of samples of grade 1 TNT.

#### Nitric Ester Research

UNCLASSIFIED

In continuation of partial nitration studies of polyhydric alcohols, trimethylolethane (metriol) was nitrated, using mixed acid containing 1.6 equivalents of nitric acid per mole of alcohol; the products were metriol trinitrate (a viscous oil) and a water-soluble solid (crystallised from benzene, m.p.  $75^{\circ}\text{C}$ ). The latter and its p-nitrobenzoate, m.p.  $146^{\circ}\text{C}$ , are being analysed.

The possibility of improving yields of partial nitric esters by performing nitrations in a two-phase system of mixed acid and methylene chloride is being investigated.

#### Nitramine Chemistry

RESTRICTED

Study of nucleophilic displacement reactions involving the acetoxyl group of six-, seven- and eight-membered ring N-acetoxymethyl nitramines has been completed.

The acetoxyl group of 3-acetoxymethyl-1,5-dinitro-1,3,5-triazacycloheptane is readily displaced by a variety of nucleophilic reagents including alcohols (ethanol, methanol, ethyleneglycol), sodium cyanide, sodium azide, acetyl chloride and primary nitramines (methyl-, butyl-, methylenedi- and trimethylenedinitramine). Determination of elemental composition, infrared spectra and, in some cases, molecular weight, enabled structures to be assigned to products of nucleophilic displacement. Further information was obtained by studying reactions of the compounds with water, alcohols, amines, acetyl chloride, acetic acid/sodium acetate, acetic anhydride and nitric acid.

Ether dilution of nitrolysis mixtures gave an unstable solid which reacted with methanol to yield 3-methoxymethyl-1,5-dinitro-1,3,5-triazacycloheptane suggesting that reactions of nitric acid with 1,5-dinitro-1,3,5-triazacycloheptane derivatives may involve formation of a nitroxymethyl intermediate.

Treatment of 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (I) and 1-acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetra-azacyclo-octane (II) with sodium cyanide or sodium azide led to decomposition and gave either no product or a trace of 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetra-azacyclo-octane (DPT). Attempted self-condensations of I and II failed, although this is a typical reaction of the seven-membered ring acetate.

/Alcohols .....



Alcohols reacted with I and II to yield the corresponding six-membered ring ether, 1-alkoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane. Some interconversions of these ethers were performed.

No bicyclic nitramines possessing six- or eight-membered rings were obtained when the acetates I and II were allowed to react with difunctional primary nitramines in acetone or dimethylformamide.

When I was treated with ethylenedinitramine in acetone/pyridine or in alcohol, the products were derivatives of triazacycloheptane: 1,6-bis(3,6-dinitro-1,3,6-triazacycloheptyl)2,5-dinitro-2,5-diazaheptane and 3-alkoxymethyl-1,5-dinitro-1,3,5-triazacycloheptane respectively. Compound II behaved similarly with ethylenedinitramine in hot alcohols. Both acetates (I and II) reacted with trimethylenedinitramine in alcohol to yield a new, monocyclic nitramine, 3-alkoxymethyl-1,5-dinitro-1,3,5-triazacyclo-octane; with methylnitramine in methanol both acetates gave tris(N-nitro-N-methylaminomethyl)amine.

Sodium nitrite in sulphuric acid converted the six-, seven- and eight-membered ring acetates into 3,5-dinitro-1-nitroso-1,3,5-triazacyclohexane, 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane and 3,5,7-trinitro-1-nitroso-1,3,5,7-tetra-azacyclo-octane respectively.

#### Non-aqueous Titrations of RDX and HMX

UNCLASSIFIED

Although it is well-known that RDX and HMX behave as acids in a variety of non-aqueous solvents, consuming respectively three and four equivalents of base (e.g. sodium methoxide), no attempts have been made to determine the fate of the nitramines during the titrations.

Preliminary experiments show that although both titrations are irreversible, the reactions involved are not identical. Sodium nitrite is a common product but only HMX yields the sodium salt of methylenedinitramine, identified by conversion into the copper salt, which was also prepared directly from methylenedinitramine.

Work is in progress to characterise other products and to establish a nitrogen balance for the reaction.

#### Substituted Hexamines

CONFIDENTIAL

As part of a general investigation involving the nitrolysis and nitrosation of N-substituted derivatives of hexamine some preliminary studies have been made of reactions between hexamine and difunctional alkyl halides. Hexamine reacted with diiodomethane in methanol to yield a compound, m.p.  $173^{\circ} - 176^{\circ}\text{C}$  (decomp.), with elemental composition corresponding to the quaternary salt  $[(\text{CH}_2)_6\text{N}_4]_2\text{CH}_2.\text{I}_2$ ; a small amount of methylhexamine iodide was also isolated. The chief product was obtained as large colourless prisms which decomposed in water and gave diiodomethane.

/1.2 .....



1.2 PILOT SCALE PRODUCTION. INVESTIGATION OF PROCESSING METHODS

Isocyanates

CONFIDENTIAL/DISCREET

Laboratory and plant studies on the preparation of 3-nitrazapentane 1,5-di-isocyanate have been completed, and 7 lb. of pure material made, on the facility described in TR.2/63. The plant consisted basically of a 10 litre reactor, fitted with stirring and brine cooling, and a 10 litre distillation flask with an intervening separator so that the last two stages, the preparation of the acid azide in the reactor and its decomposition to isocyanate in the still, could be run consecutively by remote control. The first installation had a large separator with an arrangement so that the chloroform solution of organic acid azide could be washed several times with water. It was subsequently found possible to make good purity isocyanate in good yield without washing and drying and the process was simplified by introducing a continuous separator to reject any aqueous layer present in the chloroform layer being transferred to the still. The same apparatus with simple modifications was also used for some of the earlier stages of the synthesis such as nitration to the nitramine, and preparation of the acid chloride. The project has been a valuable exercise in remote control of a complicated and unusually dangerous process in relatively cheap and quickly assembled large laboratory glassware with simple instrumentation and optical viewing. Information on heats of reaction and gas evolution has been obtained, and further scale-up could be made safely.

As part of this process the removal of water and alcohol from chloroform with molecular sieves has been investigated in the laboratory and developed to plant scale, and the final purification of the isocyanate was carried out in a short path vacuum still.

2-Nitroethanol

UNCLASSIFIED

The process selected comprised four stages; the reaction of para-formaldehyde with nitromethane catalysed by alcoholic potassium hydroxide, the neutralisation of the catalyst with sulphuric acid, a primary distillation to remove the large excess of nitromethane used in the reaction, and a distillation of the residue at 1 mm mercury to recover nitroethanol from the by-products. Earlier work had indicated that the explosion hazards were principally associated with the distillation stages, and considerable modifications were made to the process to design out the hazards on the pilot plant.

The primary distillation apparatus was designed for continuous, semi-automatic operation employing a falling-film tubular evaporator with temperature limited to 100°C. This had a capacity of 40 lb/hr. when tested on a liquid mixture of 90 per cent isobutanol and 10 per cent diethylene glycol. The cyclone separator gave excellent residue and distillate separation, the residue containing only 5 per cent of volatiles. An automatic valve on the feed starts the distillation when the pressure drops to 10 cm mercury. The second distillation stage apparatus is batch operated and "open" steam heating is used to avoid surface temperatures higher than 100°C which might initiate a runaway thermal decomposition. A specially designed still has been constructed with a counterbalanced blow-off top surmounting a 6-inch diameter still-head. Remote operation is arranged for both stages.

/Several .....



Several batches have now been made, each having a charge of 200 lb. of nitromethane and 10 lb. of paraformaldehyde. Deviations from laboratory experiments have been noted during the reaction stage: the extent of reaction is thought to be influenced by the initial nitromethane temperature and by raising this in the last run an increase in the conversion to nitroethanol has been achieved. The rate of feed to the primary distillation is 25 lb/hr. giving approximately 25 lb. of residue after 9 hr. distillation. This residue yields 5 lb. of nitroethanol in the second distillation. The purity of the product as determined by infrared absorption and by nuclear magnetic resonance analyses indicates close similarity to the laboratory product.

Decomposition occurred as expected. At the beginning of the second distillation a considerable volume of gas is evolved so that even with a powerful vacuum pump with a swept volume of 30 ft<sup>3</sup>/min. the pressure remains at 20 - 30 mm mercury. Thus, in the absence of cooling by evaporation, the still contents tend to reach the temperature of the heating medium and if this is not restricted, the danger level of 130°C might be reached. The situation is similar at the end of the distillation; there is evidence of decomposition in the form of oxides of nitrogen emitted from the outlet of the vacuum pump, as well as the pungent liquid recovered from the Drikold traps; but at no time was there evidence of uncontrolled decomposition during either distillation, whereas in pilot scale operation reported in the American literature explosions occurred. Also, the use of the diluent diphenyl ether in the second distillation has been avoided. These advances were made by studying the thermal stability of the system, and designing the stills accordingly; and it is considered that the stability apparatus used could be applied with advantage to other reactions both within and outside the field of explosive and propellant manufacture.

#### Ammonium Perchlorate

RESTRICTED

The application of the Microniser fluid energy mill in grinding ammonium perchlorate to a specific surface of 15,000 - 20,000 cm<sup>-1</sup> was investigated in a series of test runs. The quality and size reproducibility were shown to be satisfactory. The hazard arising from build-up of static electricity on the dust collecting stocking, which might cause a fire, was examined; this led to the provision of an earthed ring of static discharge chains hung in contact with the outside surface of the exhaust stocking, and arranging a limited degree of remote operation. A further practical point is that the air used may need to be of low humidity, since a tendency was observed for the very finely divided ammonium perchlorate to cake and bridge across the mill outlet if the grinding air was moist. Successful operation was achieved, particularly in cold weather when the compressed air was of low humidity, but some further experimentation would be necessary to determine the correct humidity level.

#### Catalysed Ammonium Perchlorate

CONFIDENTIAL

Some work was started to prepare crystals of ammonium perchlorate containing a burning rate catalyst such as copper nitrate or similar compound. Tests were made to prepare 'dirty' crystals, with many inclusions of impure mother-liquor, but it was not possible to occlude more than 0.01 per cent of copper into a crystal by such physical means. Crystallisation from a suspension of finely ground copper chromite or copper oxide produced the

/surprising .....



surprising result of good crystals free of inclusions. Another possibility was to co-crystallise a coordination compound of a catalytic metal with ammonium perchlorate, but examination of the molecular volumes of the ions concerned indicated that the solvated copper ion which is associated with four water molecules is unlikely to enter the crystal lattice of ammonium perchlorate. The best result was obtained by using a physical mixture of ammonium perchlorate and cuprammonium perchlorate. The latter forms azure blue crystals which appear to be stable when exposed to the atmosphere and which are not as sensitive to friction as the corresponding cuprammonium chlorate.

Guanidine perchlorate was prepared and submitted for safety testing, but attempts to co-crystallise copper compounds with this material were unsuccessful.

/2 .....

2.1 EVALUATION

2.1.1 Analytical

The Determination of RDX in Propellant Compositions

UNCLASSIFIED

It has been found that RDX can be removed from a casting powder by prolonged extraction with dichloromethane. The rate of extraction appears to depend on the state of gelatinisation of the propellant matrix.

RDX is precipitated quantitatively from the dichloromethane extract by the addition of petroleum ether (40 - 60°), and is determined in dimethyl formamide solution by titration with sodium methoxide to an Azo-Violet end point\*. Nitroglycerine, 2-nitrodiphenylamine and resorcinol interfere with this titration.

\*Kaye. Picatinny Arsenal Technical Report No. 8.

Determination of Residual Solvents

UNCLASSIFIED

In collaboration with other members of D.C.I.'s Propellants Analysis Working Party, Panel D, methods for the determination of residual solvents and water in casting powders and cellulose acetate sheet are being examined. Members of the Panel obtained a fair degree of agreement in tests on standard samples, using a method devised by N.O.I.L. Caerwent. This consists essentially of softening the powder or cellulose acetate with a suitable solvent, distilling off the solvent, thus removing the volatile constituents of the sample, and examining the distillate by gas-chromatography.

Discrepancies between the results obtained by the members of the Panel are thought to be due to variations in the methods used to determine calibration factors for the chromatogram. To check this point further trials are proposed in which mixtures of solvents, simulating the distillates obtained from samples, will be circulated for analysis.

Some improvement in the results for water was obtained by using columns with PTFE or Kel F as the stationary phase support instead of "Embacel". However, columns packed with Carbowax 1500 on PTFE deteriorated rapidly, considerable softening of the support being observed. Kel F is superior in this respect.

Collaboration with N.A.T.O.

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In conjunction with N.O.I.L. and D.C.I., and other laboratories in N.A.T.O. countries represented on Limited Sub-Group E, AC/60, a standard sample of single-base powder stabilised with diphenylamine was subjected to the proposed N.A.T.O. surveillance test. The purpose of this test is to confirm the stability of propellants for a period of 5 years in magazine storage at 30°C. This confirmation is obtained by a heating trial at 65.5°C for 60 days, the stabiliser content of the propellant being determined before and after heating.

/Two .....



Two methods of analysis were employed, both involving separation of the stabiliser by steam distillation, followed in one case by a gravimetric determination, and in the other by a spectrophotometric estimation. Agreement between laboratories was not good, but not sufficiently poor as to preclude the usability of the test. The principal cause of discrepancies in the results seems to have been a failure to control the heating temperature sufficiently closely. Also, the results obtained by the spectrophotometric method of analysis were affected by the variations in the amounts of diphenylnitrosamine converted to diphenylamine during distillation. Since these two compounds have extinction coefficients which differ considerably, appreciable errors occurred, which could have been avoided by refluxing with alkali before distillation to ensure complete conversion to diphenylamine. With this modification, the method would be preferable in many circumstances to the usual gravimetric-bromination method.

#### 2.1.2 Compatibility, Stability and Climatic Testing

##### Investigations of Reactions Occurring Between Stabilisers and Nitric Esters CONFIDENTIAL

The rate at which resorcinol is consumed when heated with nitroglycerine has been further studied. Results have confirmed that a considerable proportion is lost by reactions other than with oxides of nitrogen produced by thermal decomposition of nitroglycerine. However, the obtaining of satisfactory quantitative results has been hampered by the limitations of the available analytical methods, and these have had to be improved. The method for resorcinol given in E.R.D.E. 26/R/62 has been critically examined and optimum concentrations of the reagents to produce maximum sensitivity determined. Similar work is in hand to improve methods for determining diphenylamine and the other stabilisers.

##### Compatibility of Brass Cartridge Cases

CONFIDENTIAL

The trials mentioned in Section 2.1.2 of E.R.D.E. TR.2/63 are continuing. Incompatibility between brass and double-base propellants results in the formation of large quantities of brown condensate on the brass surface, and in a considerable fall in the stabiliser content of the propellant. The condensate consists principally of nitroglycerine, its sensitiveness being between that of DEGN and NG.

Although several trials have yet to be completed, the following conclusions can be made:

1. Chromate passivation does not affect the compatibility of the brass surfaces.
2. In most cases the incompatibility is a property of the brass surface. Removal of the surface layer by machining produces a compatible surface. There has been only one exception to this, newly machined surfaces of brass used at R.O.F. Birtley showed some degree of incompatibility.

/3. ....



3. Current cartridge case production uses a phenol-formaldehyde lacquering process but this is ineffective in preventing incompatibility. However, laboratory tests have now shown that this lacquer can be applied satisfactorily and prevent incompatibility.
4. Gun propellants vary in the degree of incompatibility towards cartridge brass. Cordite SC is more incompatible than cordite N. Tests of other cordites are being made.
5. The seriousness of this incompatibility under service conditions is not great, and ammunition would have to be kept under extreme conditions of heat for fairly long periods before condensation occurred. It does however, suggest a new possible explanation for the formation of nitroglycerine condensates in ammunition, which has caused concern from time to time.
6. This is not a new situation, cartridge cases made in 1940 behave similarly.

Compatibility of Epophen Cements used in Carl Gustav 84 mm Ammunition

CONFIDENTIAL

Epophen cement E.L.5 with Hardener EHM4 has been used in direct contact with the double-base propellant charge and ballistite igniter of this ammunition. Initial tests at N.O.I.L. Caerwent indicated that the cement was moderately incompatible and that the hardener was extremely so. However, tests in this Establishment have shown that the correctly mixed cement is compatible with the propellant, but there is no doubt as to the extreme incompatibility of the hardener. The safe life of this ammunition is therefore dependent on the correct mixing of the cement, and this is a factor which is difficult, if not impossible, to control by normal inspection methods.

Another Epophen cement formulated with a different, but compatible, hardener (resin EL5 + hardener EHR1), with very similar adhesive properties has been found, and the use of this material in the ammunition is being advocated very strongly. It is of interest that this is the only cold setting, epoxy cement, so far encountered, which fully meets compatibility requirements for use with colloidal propellants.

Oxidation of Nitroso Derivatives of Diphenylamine using  $H^{15}NO_3$  UNCLASSIFIED

The previously reported study (TR.2/63) of the oxidation of 2,4-dinitrosoresorcinol to 2,4-dinitroresorcinol using labelled nitric acid has been extended to N-nitroso- and 4-nitrosodiphenylamine. However, treatment of the latter with nitric acid did not yield 4-nitrodiphenylamine. Products so far identified are 4,4'- and 2,4'-dinitrodiphenylamine. It is believed that 4,N-dinitroso- or 4,4'-dinitroso-diphenylamine is the first product. Authentic samples of these are being prepared and characterised.

In another approach to elucidate the mechanism the corresponding reactions of N-methyldiphenylamine are being investigated. 4-nitroso- and 4-nitro-N-methyldiphenylamine are at present being prepared and characterised together with polynitro derivatives which may result from further nitration.

/In .....



In the corresponding reaction of N-nitrosodiphenylamine with nitric acid, 2- and 4-nitro-diphenylamine are the first products isolated. No C-nitroso compounds were isolated.

Use of Thin Layer Chromatography in Stabilisation Studies

UNCLASSIFIED

(a) Identification of diphenylamine nitro and nitroso derivatives.

Small thin layer chromatography plates (coated microscope slides) have been used extensively in the separation and identification of nitro and nitroso diphenylamines. A spray reagent (strong aqueous/alcoholic KOH) has been developed which gives characteristic colours with most of the compounds studied. In some cases HCl vapour and NH<sub>3</sub> vapour have been shown to produce characteristic colours also. Two dimensional development as used recently by Yasuda on diphenylamine systems has also proved of considerable value.

(b) Reactions in the adsorbent layer.

Reactions of diphenylamine derivatives have been studied in the adsorbent layer. Exposure of a spot on a plate to HNO<sub>3</sub> vapour, nitrous fumes or N<sub>2</sub>O<sub>4</sub> for a minute or two followed by development in the normal way gave the same products as similar reactions done in solution over a much longer period of time. This method is particularly convenient for preliminary investigations of reactions where several products might be expected.

Some success has been achieved in separating larger quantities of materials using a simple coating technique not involving any special equipment.

Reactions of Stabilisers with Free Radicals

UNCLASSIFIED

Further work has been carried out on the reactions of tertiary butoxy-radicals with diphenylamine and resorcinol at 85°C for 3 days.

Samples of the green materials obtained with diphenylamine have been examined by physical and chemical methods, and these show that they are complex polymerisation products of diphenylamine with molecular weights of approximately 700.

High-temperature reactions of diphenylamine and tetraphenylhydrazine with some oxidising agents and catalysts were shown to produce similar green products with molecular weights of approximately 1000.

Purification of these materials by normal solvent methods has proved difficult and thin-layer chromatography has been applied. Separations were obtained on flat plates, but improved separations were effected by the use of a thin layer coating of Silicagel G on spheres and a mixture of monoglyme/cyclohexane as developing agent.

In both cases, however, it was found that these materials were very sensitive to light when solutions were added to the Silicagel G, and therefore additional experiments at 85°C have been started with mixtures of ditertiary dibutyl peroxide and diphenylamine and of the peroxide and resorcinol with light being excluded.

/2.1.3 .....



### 2.1.3 Calorimetry

#### Strand Burner Investigations

RESTRICTED

At the request of the Panel on the Control of Quality of Rocket Propellants, attempts have been made to improve the reproducibility of the strand burning test. Repeat determinations of rates of burning of PU, VU and SC over periods of several weeks showed that, in general, the reproducibility within any one day was satisfactory, but that considerable variations in burning rate were obtained from day-to-day with PU and VU propellants (SC being less prone to these variations). Attempts were made to correlate these day-to-day variations with a wide variety of factors, such as residual methylene chloride content (from the inhibiting solution), laboratory temperature and humidity, but without success. The viscosity of the lacquer solution used for inhibiting was found to have some effect (typically, 1/2 per cent on burning rate over specified viscosity range). Burning rate measurements on strands dipped daily in fresh solution prior to firing and on strands dipped in solution in current use (and up to 3 weeks old) indicated that reproducibility was improved by the use of fresh solution. In view of this effect, R.N.P.F. and N.O.I.L., Caerwent have been advised to change their dipping solutions at not longer than weekly intervals. (R.O.F. and D.C.I., Bishopton already comply with this.)

Changes in the inhibiting and conditioning procedures were found to have no beneficial effect. So far, the procedure found to give the lowest variability (within-day and day-to-day) with PU and VU propellants is that of burning uncoated strands under oil. The values obtained are lower than by the present technique, particularly at pressures at which mesa type burning occurs.

#### Heat of Formation of Di-Tertiary Butyl Peroxide

UNCLASSIFIED

A sample of di-tertiary butyl peroxide, supplied by Messrs. L. Light and Co., Ltd., was water washed to give a purity of better than 99.5 per cent.

Heat of combustion measurements at 25°C were carried out on this purified sample, and the following figures are based on the mean of three determinations:

Heat of combustion	-1276.1 kcal/mole
Heat of formation at constant pressure	-91.2 kcal/mole
Heat of formation at constant volume	-85.1 kcal/mole

#### Heat of Combustion of Teracol 30

Heat of combustion measurements at both 25°C and 45°C have been carried out on a sample of Teracol 30 (N.W.2540), a linear polyester produced from tetrahydrofuran obtained from Messrs. DuPont Ltd.

/Heat .....

Heat of combustion of solid polymer at 25°C:

the mean of six determinations gave

$$= -317.83 \pm 0.62 \text{ kcal/100 g.}$$

Heat of combustion of liquid polymer at 45°C:

the mean of five determinations gave

$$= -319.17 \pm 0.13 \text{ kcal/100 g.}$$

The heat of polymerisation was calculated to be  $12.7 \pm 1.1$  kcal/100 g. and the heat of fusion of the polymer, 1.3 kcal/100 g.

#### 2.1.4 Mechanical and Rheological

##### Dimensional Stability of Large Cordite Charges

RESTRICTED

Extruded cordite, particularly in large charge sizes, is not dimensionally stable but shows a progressive change in length, even at ambient temperature, due to slow relaxation of the stresses locked in by the extrusion process. Such stresses might distort a charge to unacceptable dimensions or even cause a charge to fracture.

Measurements of the change in dimensions with time of Gosling charges have been made at R.O.F. Bishopton and R.N.P.F. Caerwent over periods of up to six months. The results of these tests have now been analysed at E.R.D.E. in terms of the known rheological behaviour of cordite.

An empirical equation has been found which describes the rate of the annealing process and its dependence on temperature. The effect of increasing the temperature is merely to accelerate the annealing process and not to release additional locked-in stresses. The relaxation rate at 60°C is more than 120 times that at 20°C; an appropriate temperature coefficient, of the activation energy type, has been determined.

After six months at ambient temperature, the shrinkage rate of a Gosling charge is only about  $10^{-9}$  inch/inch minute, but there is no indication that final equilibrium would be reached even after several years, and it is not possible to deduce from the measurements what the final unstrained dimensions would be. Other evidence suggests that the total strain initially built into the charge is between one and two per cent, and that about half of this is removed by annealing for three days at 60°C.

##### Tensile Studies on Low Modulus Polyurethane Propellant

UNCLASSIFIED

Tensile tests have been carried out on a polyurethane propellant of abnormally low modulus, having a tensile strength, as determined by the standard routine method, of only 24 p.s.i. at 25°C.

/Values .....



Values of strength and modulus at various rates of strain and at normal and elevated temperatures were determined, and the results compared with gravitational and set-back stresses set up in actual or projected motor systems. In most cases, the strength of the propellant was found to be adequate, and there would seem to be a good case for developing low strength rubbery propellants since the consequent gain in extensibility should lead to improved low temperature behaviour.

The problem of falling acceleration stresses on a burning rocket charge was considered. During burning, acceleration stresses will diminish in an approximately linear manner as the propellant is consumed, but current knowledge of fracture behaviour is insufficient to enable the resistance of a propellant to a steadily diminishing load to be calculated from data referring to strength under constant load. An apparatus was therefore devised with which a tensile test piece could be subjected to a diminishing load applied by a leaking can of water. It was found that the low modulus polyurethane propellant could withstand an initial stress some 20 to 30 per cent greater than the constant stress which would produce fracture in the same time.

#### The Tensile Strength of Polyisobutene

UNCLASSIFIED

Polyisobutene (PIB) the binder for plastic propellant, is a visco-elastic liquid. At low shear rates it is a Newtonian liquid with little or no strength; at high shear rates it has considerable strength, and can be drawn into long tenacious threads. A knowledge of the strength of these threads is required for interpreting plastic propellant rheology but previous attempts to measure the strength of PIB were unsuccessful, except at temperatures below  $-60^{\circ}\text{C}$ .

A method has now been devised in which threads are drawn out by a falling steel ball. The experiment is carried out in a dark room, illuminated by a Strobflash unit 160 times per second. A series of magnified shadow pictures of the strand is recorded with a cine camera, and a series of dots representing the specular reflexion from the ball is recorded with a still camera. The ball falls slightly slower than it would under gravity and, from the rate of fall, the stress in the strand can be determined as a function of strand length.

The final strands are about 150 cm long and  $10^{-3}$  cm diameter. The tensile pull is about 0.5 gramme. The strength of the PIB is approximately 500 p.s.i. at  $20^{\circ}\text{C}$  and a strain rate of  $160\text{ min}^{-1}$ . This surprisingly high value, when subjected to time-temperature superposition treatment, is in excellent agreement with values obtained at low rates, and temperatures below  $-60^{\circ}\text{C}$ .

#### Cracking of Charges by Thermal Gradients

CONFIDENTIAL

A study was started some time ago to investigate the conditions under which a propellant charge might fail due to transient thermal stresses. Shortly after the work was started, failure of CDB Bullpup charges during temperature cycling was reported, and our effort is now concentrated on this particular problem.

/Barlier .....



Earlier photoelastic work has been reanalysed and extended so as to give the strain levels as well as the stress distribution in thermally stressed charges. In the absence of stress concentrations, the strain levels were found to be in agreement with those calculated from the known thermal properties of the material. It was established that propellant fracture would occur at the same strain level irrespective of whether the strain was imposed thermally, or mechanically. This correlation was obtained with the Bullpup propellant using bend tests to establish mechanically imposed strain capability at low temperatures, and a special test piece, with a geometry which enables large thermal strains to be obtained, to give the thermally imposed strain capability.

Transient thermal strains are very low and rarely exceed 1 per cent, so that a propellant must be very inextensible to fail under thermal stressing. In one experiment a 2 inch rocket charge in cordite PU withstood a temperature gradient due to maintained temperatures of  $-70^{\circ}\text{C}$  in the conduit and  $25^{\circ}\text{C}$  on the outer surface. However, the extensibility of the Bullpup propellant at  $-40^{\circ}\text{C}$  is only about 1 per cent, whereas PU has an extensibility at the same temperature of about 4 per cent.

A factor which might well be expected to contribute to the weakness of the Bullpup charge is that the conduit has very sharp corners. Notched bar impact tests have therefore been carried out to assess the significance of this factor. Notches were used with tip radii varying from 0.00 inch to 0.06 inch. With cordite CU, this change in radius gave a fourfold increase in impact strength, but with the Bullpup propellant the increase was only 10 per cent.

Impact tests were also carried out on a series of samples of OIY propellant having various depths of notch; this test system has previously been used with cordites to compare the stress raising effects of notches. The specific impact energy (impact energy/fracture area) of OIY was found to be independent of notch depth over the range of notches studied, whereas, over the same range, the value for cordite VU varies threefold. This result, taken in conjunction with the earlier discovery that root radius has very little effect, confirms the view that the sharpness of the corners cannot be the only reason for the cycling difficulties with the Bullpup motor.

Evidence was then sought that the charge contained internal stresses; the technique used was similar to that used in investigating stressing in large extruded cordite charges. Saw cuts were made successively at various points in a section from an I.M.I. charge, and changes in the gap thickness, and in the overall dimensions of the charges were accurately measured. As successive webs were cut, the gaps closed up, indicating that internal tensile stresses were being relaxed. When the individual rings were separated, the two inner rings recovered their original dimensions, while the outer ring continued to shrink, until its perimeter was reduced by more than 16 mm. This represents an internal circumferential strain of about 1.3 per cent, which is a high proportion of the low temperature strain capability of the propellant. A load of more than 6 lb. per inch length of charge is necessary to close the gap. The strain will tend to concentrate at the inner corners of the outer ring, and it is at these corners that failure always begins on temperature cycling.

/2.1.5 .....



#### 2.1.5 Charge Defect Detection

##### Examination of Charges by Radiography

CONFIDENTIAL

A total of 26 rod-and-tube E.555 (prototype Chow) and E.557 (Chow) charges have now been inspected on behalf of I.M.I. (Summerfield). On the basis of this work a decision has been taken by the firm to employ two-step casting for the first phase of motor performance evaluation.

The sensitivity of this inspection has been investigated using an E.555 rod charge with holes of various sizes drilled in the centre and outer propellant. At the maximum operating voltage of 300 kV, a single 0.075 inch diameter hole could just be seen in the outer propellant, and a 0.125 inch diameter hole in the inner propellant, corresponding to sensitivities of 0.75 per cent and 1.25 per cent respectively.

Attempts to radiograph polyurethane propellant filled 24-inch diameter Phoenix boost and sustainer motors showed them to be beyond the range of the present 300 kV set.

##### Ultrasonic Inspection of 9-inch Solid Double-Base Propellant Charges

CONFIDENTIAL

Semi-automatic inspection has been set up, with the probes moving linearly, and the charge rotating, to produce either longitudinal or diametral scanning in a spiral path. Several 9 to 10-inch diameter solid double-base charges have now been inspected, including PU pressed at Caerwent, TU from Dishopton (for a Norwegian order) and Australian Ikara sustainer charges.

With solventless extruded cordite the effects of a steamer plate or spider are not apparent on a linear scan but are easily seen on a diametral scan which shows a band of oscillations of the order of  $\pm \frac{1}{2}$  db. This could prevent the detection of a very small flaw, but sensitivity will be in the region of 1 per cent. Axial inspection will only detect large flaws as the observed trace varies by  $\pm 2$  db owing to phase changes and mode conversions of the beam by reflections at stream boundaries as the charge rotates.

With cast double-base propellant charges, both diametral and axial scanning have been of value in assessing charge quality. Ultrasonic methods are to be preferred to radiography in detecting porosity. 'Noise' levels, from electronic and propellant sources, increased with propellant thickness but with the E.R.D.M. Mk.III set thicknesses of up to 14 inches can be examined. When both scans can be made, the position of voids can be determined and processing methods modified to eliminate them.

Experimental 9-inch diameter charges made in Australia for Ikara motors have been inspected satisfactorily using the Mark III set and porosity shown to be present in certain areas. Measurements have been made to correlate attenuation changes with density of test pieces.

/2.3 .....

## 2.3 COMBUSTION AND ASSOCIATED PROBLEMS

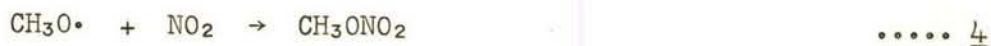
Gas-Phase Reactions of Nitric Oxide and Nitrogen Dioxide with Free Radicals  
UNCLASSIFIED

Studies on the reactions of methyl and methoxyl radicals with nitric oxide and nitrogen dioxide, using the acetaldehyde/nitrogen dioxide system as radical source (TR.1/63), are virtually complete, and a paper is being presented at the Discussion on Elementary Combustion Reactions being held at the Xth International Combustion Symposium at Cambridge in August 1964.

The kinetics of the two competing reactions of methyl radicals with nitrogen dioxide



have been established by relating them to the known rate-constant for reaction 10 of methyl radicals with nitric oxide. At 50 - 90°C, with third-body pressures below about 100 mm Hg, 1 is in the transition stage from second to third-order, but at higher pressures it is second-order with  $K_1 = 1.7 \times 10^{12} \text{ mole}^{-1} \text{ cm}^2 \text{ sec}^{-1}$ , whilst 2 is second-order with  $K_2 = 3.3 \times 10^{12} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ . The activation energy difference  $E_1 - E_2 = 0$ , so that  $E_1 = E_2 = 0 \text{ kcal mole}^{-1}$  because 1 is a radical association reaction. From the relative rates of formation of methyl nitrite and nitrate

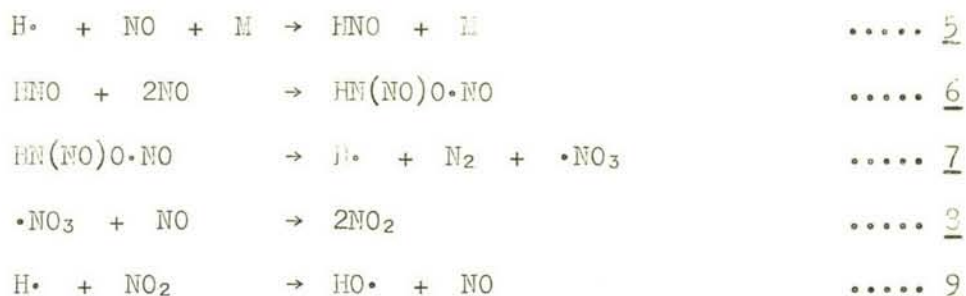


$$K_3/K_4 = 1.8.$$

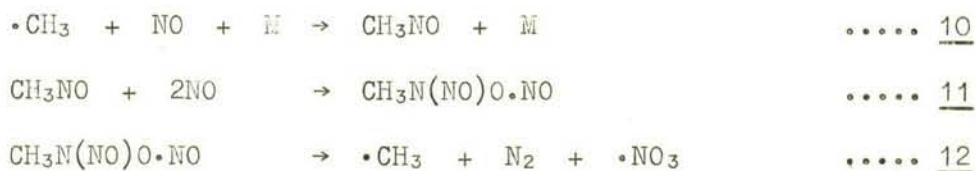
The extension reduction and oxidation of nitric oxide to nitrogen and nitrogen dioxide reported (TR.1/62) in diethyl peroxide/nitric oxide systems at 95°C, has now been shown to be probably due to reactions of nitroso-methane, and not nitroxyl as previously suggested, with nitric oxide. Large yields of nitrogen and the dioxide are always accompanied by carbon dioxide, which, together with methyl radicals, is formed by reaction of the small amounts of nitrogen dioxide formed from the nitroxyl/nitric oxide system, 6, 7, 8, with acetaldehyde. Methyl radicals then react with nitric oxide via 10, 11, 12, to produce large yields of nitrogen and the dioxide by a chain mechanism. Calculations using known rate-constants show that the nitroxyl/nitric oxide system cannot support chains,

/Equation 5 .....





because hydrogen atoms formed in 7 are removed as rapidly by termination, 9, as by the propagation reaction, 5, so that large yields of nitrogen and the dioxide are impossible. The nitrosomethane/nitric oxide system, on the other hand,



can support chains because methyl radicals, regenerated in 12, are removed much more rapidly by propagation, 10, than by the termination reactions 1 and 2.

#### 2.4 EXTRUDED PROPELLANTS

##### Modified Compositions

CONFIDENTIAL

The slow burning hot propellants developed for E.T.316 are platonised over the pressure range, 400 to 600 p.s.i. Attempts have been made to extend the plateau up to 800 p.s.i. but any extension of the plateau to a higher pressure has been accompanied by an increase in the rate of burning.

Modification of propellant AU by the use of pyro nitrocellulose in place of wood nitrocellulose lowered the peak rate by up to 0.10 inch/sec. It was confirmed that altered amounts of ballistic modifiers would produce a satisfactory ballistic match for AU propellant.

Strand burning rates of about 1.5 inch/sec over the pressure range 2500 to 4000 p.s.i. have been achieved by the addition of 0.6 parts of Dixigloss carbon black or 0.15 parts of activated Dixigloss in place of Ukarb 340 in propellant F.488/1225.

##### Propellants for Dual Thrust Rockets

CONFIDENTIAL

The drawback of the extruded dual propellant charge solution of E.T.316 is that the sustainer propellant burns at pressures above its plateau while the boost charge is burning. The sustainer propellant has a relatively high pressure exponent at the boost-pressure and modifications to the composition have not indicated any means of reducing it.

/Dual .....

Dual pressure 3-inch motor firings have been conducted with tubular charges made from F.547/371 (sustainer) and two boost propellants with wide plateau limits (2000 to 3000 p.s.i.). Reproducible and stable ballistics were obtained without excessive pressures although the sustainer propellant was burning well outside its plateau limits. The major problem is the somewhat large temperature coefficient (0.35 per cent per °F) for pressure during the boost firing, even though burning time is little affected by temperature. Pressure differences were slightly less with KU than F.488/1480 but the energy level of the former is 150 cal/g. lower. The temperature coefficient for the sustainer was normal for pressure and probably acceptable on burning times of about 7 seconds.

#### Propellants to Resist High Temperatures

CONFIDENTIAL

Ejector release units require propellants which are resistant to temperatures of up to 135°C for short periods; temperatures of 150°C and 200°C may be experienced in the future. Testing conditions have been standardised; 30 g. of propellant in a steel E.R.U. cartridge case is stored into a thermostatically controlled hot air oven. At 130°C, SC cordite ignites in 2 hours, picrite cordite (MNQF) in 4 hours and single base propellants in 9 hours. Attempts to improve the resistance of the latter by change in the stabiliser had negligible effect. The addition of 10 per cent plasticiser had a deleterious effect, but the addition of 5 per cent of picrite and 5 per cent plasticiser gave a time to ignition at 130°C of 44 hours. Improvement was still noticeable at 135°C where the comparative time was 5 hours against 3½ hours, but at 140°C there was little difference.

These results indicate that modified single base formulations will meet Service requirements involving periods of an hour or so at 135°C.

## 2.5 CAST DOUBLE BASE

### Composite Modified Casting Powder Manufacture

CONFIDENTIAL/DISCREET

Efforts have continued to increase the filler loading (aluminium and ammonium perchlorate) whilst maintaining densities acceptably close to the calculated values. Measured density has been found sensitive to the solvent used in manufacture at filler contents above 40 per cent. Ethyl acetate/diethyl ether, 80/20 (wt/wt) gives higher densities than acetone/ethanol 65/35. To maintain an average density of 97 per cent, theoretical, using acetone/ethanol, filler content must be limited to about 58 per cent whilst with ethyl acetate/ether, filler content may be increased to 68 per cent. Powder manufactures at 75 per cent filler and higher have given variable densities. Attempts to correlate the viscosity of nitrocellulose in various solvents with casting powder density have not been successful.

### High Filler Propellants

CONFIDENTIAL/DISCREET

Investigations have continued into the performance and properties of compositions containing 12 per cent nitrocellulose to explore the limitations of the CDB process more fully and to provide a background for Polaris A3 Stage 2 propellant.

/The .....



The successful manufacture of a TEGN casting powder with 75 per cent filler has enabled a high performance propellant, containing 12 per cent nitrocellulose, TEGN and increased ammonium perchlorate (F.452/448/T1) to be processed. The burning rate range attainable by alteration of ammonium perchlorate grist size only, appears to be from about 0.90 to 1.10 inch/sec at 1000 p.s.i. The measured specific impulse at 1000 p.s.i. (corrected for nozzle expansion) of 252.7 lb.sec/lb. for this composition with 55 per cent filler is 4 to 5 units higher than that normally obtained with composite modified CDB at the 42 per cent filler level. Mechanical properties at 20°C of this formulation with a maximum tensile strength of 60 p.s.i. at 57 per cent elongation and an initial modulus of about 300 p.s.i. appear marginal; usage may therefore be limited at higher temperatures unless an unusual temperature coefficient is found.

Similar compositions based on DEGN and NG/TA plasticisers which had been found too hot and erosive when fired were modified by the replacement of some ammonium perchlorate by picrite. Burning rates were found to be in the region 0.7 to 0.8 inch/sec but specific impulse was not greater than propellant containing less filler.

The mechanical properties of compositions containing NG and only 12 per cent nitrocellulose are very dependent on temperature; tensile strength falls from 24 p.s.i. at 20°C to 1 p.s.i. at 60°C. The DEGN variant is considerably less temperature dependent and although weak at 60°C, might be more acceptable for limited temperature range applications.

#### Ability to Withstand Temperature Cycling

CONFIDENTIAL

In view of current and proposed requirements to extend the useful temperature range of operation of case-bonded CDB rocket motors, tests have been carried out to assess low temperature cycling limits with simple charges with different densities of loading.

Case-bonded charges of ATN and BDI, as proposed for E.T.316, have been cast into steel long J-motor bodies, 4.8 inch internal diameter by 24 inches long, with conduit diameters up to 2¼ inches, corresponding to densities of loading from 78 per cent upwards. The ends of the charges are of a simple conical form and less liable to stress concentrations than the slotted tubular shape. The sealed motors were subjected to 10 temperature cycles:

-10°F/70°F/140°F/70°F for 16/8/16/8 hours respectively.

If no failure occurred during the first 10 cycles, the lower temperature was reduced 10°F for a further 10 cycles, and so on until failure or -60°F (the limit of available refrigeration). When there was doubt whether slight cracking had occurred a further 10 cycles was carried out to the same low temperature.

/TABLE 2 .....

TABLE 2

Conduit Diameter inches	Loading Density per cent	ATN(D27)/19 Charges	BDI(D2)/25 Charges
2¼	78	Satisfactory after cycling to -50°F	-
1½	90.3	Satisfactory after cycling to -30°F (continuing)	Satisfactory after cycling to -20°F (continuing)
1	95.7	Cracked after cycling to -20°F	Cracked after 20 cycles to -20°F.  After storage for 8 weeks at 140°F, cracked in conduit after cycling to -10°F

These results suggest that the present E.T.316 motor design is unlikely to withstand cycling below 0°F. The use of stress-relieving slots appears necessary to meet the Service requirements, but there will be a total impulse penalty.

Permeability of Inhibitor Materials to Nitrogen

RESTRICTED

Cured Hypalon CL.2759, used extensively for rocket heat insulation, has been proposed for the inhibition of CDB charges where its permeability to gas could be important. The permeability to nitrogen of samples of Hypalon prepared for bonding with Ciba Redux/Formvar film has been compared with samples prepared by the E.R.D.E. Redux/Formvar lacquer technique. The table below shows that the Ciba film treatment as used at I.M.I., leads to a permeability about half that found with the E.R.D.E. system, which is similar to cellulose acetate at higher temperatures.

Samples of experimental polyester inhibition have been found to be as permeable as cellulose acetate up to 40°C, but the lower temperature coefficients, particularly with higher silica contents (70 per cent) leads to a lower permeability than CA from 40°C to 60°C.

/TABLE 3 .....



TABLE 3

Temperature °C	Permeability to Nitrogen (ml. cm <sup>-1</sup> cm <sup>-2</sup> (cm Hg) <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>-11</sup> )					
	Cured Hypalon CL.2759				I.M.I. Unlacquered Hypalon	Convolute Wound C.A.
	E.R.D.E. Lacquer Treatment	I.M.I. Ciba Film Treatment Sample Number				
		1	2	3		
20	6.5	1.4	3.4	2.7	11.9	1.6
40	15.0	6.8	9.7	6.2	33.4	5.8
60	34.0	23.3	19.6	17.6	93.0	31.0

2.6 PLASTIC PROPELLANT

Propellants with Improved Slump Resistance

CONFIDENTIAL

A programme of work has been started to develop propellants of the plastic type with improved resistance to slumping in large motors. Initial work is concentrated on seeking improvements by modifications in binder viscosity and solids loading, by partial crosslinking of the binder, and by the introduction of gel structure by using resins soluble in the binder.

The effect of solids loading on physical properties has been studied over a concentration range of 33 to 91 per cent of ammonium perchlorate. With 91 per cent of oxidiser, the material cracked and crumbled readily; with 90.5 per cent, a coherent plastic was obtained, but reproducibility of physical properties was poor; 90 per cent of oxidiser appeared to be the maximum amount with which reasonable physical properties could be obtained.

Tests used to estimate resistance to slumping were the normal cylinder compression tests, the constant load tensile test, and the bending beam test. These were carried out at 25°C, except for the cylinder flow test which is always carried out at 60°C. Some of the results are shown in the following table.

/TABLE 4 .....

TABLE 4

% Ammonium Perchlorate	Cylinder Compression Tests				Constant Load Tensile Tests	Bending Beam Test
	P, (%)	C, (%)	F, (%)	Apparent Yield Value, ( $10^4$ dynes/cm $^2$ )	Long-time Strength, ( $10^4$ dynes/cm $^2$ )	Apparent Modulus, ( $10^4$ dynes/cm $^2$ )
88	40	80	48	4.5	4	0.2
89	19	55	31	6.5	7	0.35
89.5	14	60	13	12	9	0.55
90.5	8	35	6	14	12.5	1.0

The yield value from cylinder compression tests and the apparent modulus from bending beam tests both increase considerably with increasing solids concentration, indicating improved resistance to slumping. The plasticity values, as expected, decrease with increasing solids content so that the improvement in slumping would be obtained at the expense of poorer processing characteristics and resistance to thermal stressing. Plastic propellants already supplied to R.P.E. for trials in 3 ft. and 4½ ft. diameter motors contain 89 per cent of solids. The present work indicates that there may be scope for a further increase in solids content where resistance to slumping is of paramount importance. However, manufacturing scale effects with plastic propellants often occur, and the feasibility of making such highly loaded materials on a large scale has yet to be established.

Propellants Containing Aluminium Foil, Staple or Chopped Wire      CONFIDENTIAL

Work has started on the use of aluminium foil in place of aluminium powder to give increased burning rate. In preliminary experiments, pieces of aluminium foil of 0.0002 inch thickness and 0.5 inch width were incorporated into polyisobutene binder. During incorporation, the foil was broken into much smaller pieces (maximum size about 0.25 inch by 0.2 inch) but these appeared to be well dispersed. About 25 per cent by weight of foil could be incorporated in this way.

The dispersions have been used for preparing small batches of propellant containing up to 3 per cent by weight of foil. In comparison with the corresponding non-aluminised compositions, 1 per cent of foil increased the burning rate (at 1000 p.s.i.) from 0.72 to 1.19 inch/sec, while 3 per cent of foil gave a rate of 1.29 inch/sec. A composition containing 1 per cent of copper chromate catalyst, as well as 1 per cent of foil, had a burning rate of 1.36 inch/sec (at 1000 p.s.i.); this is the highest rate so far obtained with any E.R.D.E. plastic propellant composition.

Physical properties of the propellants containing foil appear to be satisfactory, but there is a considerable reduction in plasticity value at the

/3 per cent .....



3 per cent level (39 per cent without foil, 12 per cent with foil). The applicability of the normal plasticity test to the new compositions needs investigation but, if it is found that the reduction in plasticity is a genuine effect, and other rheological qualities are influenced in the same way, the use of foil may also offer possibility for improved resistance to set-back forces and slumping in large motors.

The enhancement of burning rate by aluminium foil is due to the high thermal conductivity of the metal and, for maximum effect, the plane of the foil should be orientated normal to the burning surface. Attempts are being made to measure the ultimate rates available from such systems by measuring the burning rates of sandwiches constructed from alternate layers of plastic propellant and sheets of foil. The progress of the flame down the metal/propellant interface and the change of contour of the burning surface are being followed photographically for burning pressures up to 200 p.s.i. With a propellant containing 89 per cent of ammonium perchlorate, the burning rate at 200 p.s.i. was trebled by the sheets of foil, and at 1000 p.s.i. the rate was doubled; the thickness of the foil had little effect.

The same propellant was made into a "swiss roll" configuration with 0.0002 inch thick foil, corresponding to a metal loading of 3.4 per cent by weight, and at 1000 p.s.i. this gave the same rate of burning as the "sandwich" construction (2 inch/sec). It was found necessary to consolidate these samples by light pressure in a mould to prevent flashdown at the propellant/metal interface.

Three different sizes of aluminium staple have been obtained from the U.S.A., the average dimensions being (1) 0.125 x 0.0045 x 0.002 inches, (2) 0.125 x 0.0045 x 0.0007 inches, and (3) 0.25 x 0.0045 x 0.0007 inches, respectively.

Propellants containing 1 per cent of each type of staple have been made, and strand burning rates compared with those of propellants containing 1 per cent of aluminium foil (0.0002 inch thick, up to 0.1 inch wide and 0.1 inch long) or 1 per cent of chopped wire (0.125 x 0.01 inch). In each case, six strands prepared by extrusion, and six strands prepared by rolling were burned at 1000 p.s.i. and the coefficients of variation determined. With normal plastic propellants, the coefficient of variation of strand burning rate is usually between 0.5 and 1.0; values above 1.0 indicate within-batch inhomogeneity. Results were as follows:

/TABLE 5 .....

TABLE 5

Composition No.	Additive	Extruded Strands		Rolled Strands	
		$R_b$ (inch/sec)	C. of V.	$R_b$ (inch/sec)	C. of V.
E 3090	None	0.724	0.77	-	-
E 4027/T1	Foil	1.192	3.36	0.965	3.68
E 4027/T3	Wire	1.021	1.53	0.951	4.32
E 4027/T5	Staple, size 1	1.190	1.83	1.193	3.17
E 4027/T6	Staple, size 2	1.094	0.37	1.097	3.18
E 4027/T4	Staple, size 3	1.062	1.86	1.070	0.77

The results indicate that with extruded strands, foil, chopped wire and the various sizes of staple all increase the burning rate to a similar extent. The extrusion process evidently gives some orientation along the length of the strand to the foil and chopped wire, but has no effect on the orientation of the staples. The generally high values of the coefficients of variation indicate considerable inhomogeneity, and means of overcoming this will be sought.

## 2.7 POLYURETHANE PROPELLANTS

### Large Scale Polyurethane Mixing and Filling

CONFIDENTIAL

The plant has continued to function smoothly. A total of 13,500 lb. of propellant has been processed since installation; ten mixes totalling 6,800 lb., since the major overhaul was completed earlier this year. The ballistics obtained were in agreement with values obtained from comparable 10 lb. and 100 lb. pilot scale batches. Burning rate tolerances of  $\pm 0.025$  inch/sec and  $\pm 0.01$  inch/sec respectively have been achieved for boost and sustainer propellants. This variation is rather greater than had been hoped for; some of it is due to differences in specific surface between different batches of ammonium perchlorate. Some of the changes in surface area during prolonged drying have been found to be due to adventitious accumulation of "fines".

A comparison has also been made of physical properties of pilot scale and large scale batches employing comparable materials; there is a trend towards propellant with higher extensions and lower tensile strengths as mixer size increases.

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In one of the early manufactures, a mix failed to cure. To avoid this, an accelerated cure test has been devised and is used prior to filling into the motor. Additional catalyst has to be added and use is made of a standardised slab mould, which gives rapid heating. Hardness of the final propellant is measured; this testing takes over an hour, rather too long for the present purpose but attempts to use the Brabender Plastograph and to measure viscosity changes prior to cure have not given a better cure potential test.

The ballistic effects of aluminium foil linings in motors have been further investigated. A 10-inch sustainer showed clearly that omission of the aluminium foil resulted in a satisfactory form to the pressure/time trace. A second foil-lined motor with a cast inhibitor ring, sealing off the foil, confirmed this conclusion.

A 5-inch tubular round, lined with Hypalon and aluminium foil has also been interrupted during burning. The propellant was found to have burned rapidly at the foil interface, and the angle between propellant and foil was about  $20^{\circ}$ . Comparison of end and radial burning showed that the enhancement next to the foil was about 2.5 fold; this corresponds well with the factor deduced by R.P.E. to account for the peaks encountered in Phoenix sustainer pressure/time curves and with simulated tests in the Strand Burner.

#### Physical Properties of U.188-type Propellants

CONFIDENTIAL/DISCREET

The addition of small amounts (ca 0.3 per cent) of C-1 diol (di- $\beta$ -cyanmethyl-2,3-dihydroxypropylamine) has been shown in the U.S.A. to result in substantial improvements in the physical properties of polyether polyurethane propellants, particularly at low temperatures. The C-1 diol reacts with the isocyanate, is incorporated into the polymer structure and is alleged to enhance bonding of the ammonium perchlorate crystals to the rubber. Marked improvements in physical properties have been obtained with L.77 polyester polyurethane propellants made at 0.85 TDI equivalence by the addition of 0.3 per cent C-1 diol. In comparison with a control, the products of the first elongations and maximum stresses were roughly doubled at 60, 25 and  $-40^{\circ}\text{C}$ .

Further work has shown that low modulus propellants (TR.2/63) made at 1.0 TDI equivalence, using modified L.77 polyester, made with 0.2 instead of the normal 0.5 mole trimethylol propane, by processing and curing at  $60^{\circ}\text{C}$  with 0.006 per cent FeAA, was often porous and undercured. This has been overcome by increasing the FeAA content to 0.015 per cent and processing and curing at  $45^{\circ}\text{C}$ , taking advantage of the fact that the urethanation reaction is accelerated more than that between the isocyanate and water, which causes porosity. Good quality propellant was obtained with fairly reproducible physical properties but mix viscosities were rather high. Typical initial moduli were about 50, 60 and 1700 p.s.i. at 60, 25 and  $-40^{\circ}\text{C}$  respectively; values for a normal U.188/L.77 composition made at 0.85 TDI equivalence are 175, 250 and 2300 p.s.i. Samples tested at 25 and  $60^{\circ}\text{C}$  did not show full recovery after test indicating that the physical properties of these propellants are intermediate between those of plastic and the normal elastomeric polyurethane types.

/Low-Temperature .....



Low-Temperature Curing: The Use of More-reactive Di-isocyanates

CONFIDENTIAL/DISCREET

Work reported in the literature on the reactivity of di-isocyanates with hydroxyl-terminated polyethers and polyesters almost invariably refers to reaction in dilute solution. It is well known that under these conditions trace impurities, apart from solvent effects, may cause misleading results to be obtained. An infra-red spectroscopic method for the determination of isocyanate reactivity with polyesters in the bulk has been developed. The strong absorption at  $4.4 \mu$ , due to the isocyanate group, of a film of premixed L.81 polyester and di-isocyanate, has been followed at  $45^{\circ}\text{C}$  in a thermostatted infra-red cell. Changes in film thickness due to shrinkage during polymerisation are allowed for by relating the isocyanate absorption to that due to C-H bonds at ca  $3.4 \mu$ . From an analysis of the kinetics of the rate of consumption of isocyanate, it was found that the times to 80 per cent reaction using 4,4'-diphenylmethane di-isocyanate (MDI) and 3-nitrazapentane-1,5-di-isocyanate (XIII isocyanate) are 5 and 8 hours respectively, as compared with 57 hours for 2:4 TDI. Contrary to results in the literature, monochlorination had little effect on the reactivity of TDI or MDI. The increased reactivity of XIII isocyanate over TDI is not in accord with American work in solution, which showed the reverse.

Several batches of U.188-type propellant have now been made at 0.85 isocyanate equivalence, using a large sample of MDI. Results previously reported (TR.2/63) on reduced curing times have in general, been confirmed, but physical properties, though probably acceptable, are not as good as with TDI propellant.

Aging of Polyurethane Propellant

CONFIDENTIAL

Two one-foot cubes, one of U.188/L.77/0.85 polyester and one of U.461/SPPG-G3000/1.07 polyether polyurethane propellants, have been examined after two years open storage in a thermostatted room at  $60^{\circ}\text{C}$ . Marked deterioration in physical properties occurred in both cases, the outer surfaces becoming almost plastic.

In the U.188 propellant, containing 15 per cent rubber, of which at manufacture only about 4 per cent was extractable (i.e. uncrosslinked); sectioning and analysis show that the extractable rubber is now 8.7 per cent at the centre of the block and 12 per cent to 13 per cent on the surface. With the U.461 propellant, rubber content 20 per cent, of which 3.5 per cent was extractable before storage the extractable rubber after storage is now 6 per cent at the centre of the block and 17.5 per cent to 19.5 per cent at the surface.

With the U.188 propellant, appreciable losses of TEGN occurred at the surfaces.

These storage conditions are, however, very severe by modern standards; in closed containers, where the supply of atmospheric moisture and oxygen is restricted, degradation would be much less.

/3 .....



LIQUID PROPELLANT ROCKET ENGINES

3.1 HYDROGEN

Point Measurements of Radiative Heat Flux from High Pressure Oxygen-Hydrogen Flames UNCLASSIFIED

Eight miniature radiation transducers were installed in the combustion chamber of a 4 cm diameter, 17 cm long, hydrogen-oxygen rocket motor, the first about one inch from the injector face, followed by others at nominal spacings of 0.5 inch and then 1 inch.

Each transducer was of 1/16 inch effective diameter and consisted of a thin metal diaphragm whose temperature was measured at the centre and at a known radius. Assuming radial heat flow, the heat flux received by the diaphragm could be evaluated from the measured temperature difference between centre and periphery, the thermal conductivity of the diaphragm, and its dimensions.

Several successful experiments were carried out at a combustion pressure of about 10 atm with a propellant equivalence ratio of 0.6, and at propellant fluxes of 2.3 and 6.9 g/cm<sup>2</sup>sec.

At low propellant flux (2.3 g/cm<sup>2</sup>sec) the radiative intensity is highest at the station closest to the injector (about 50 cal/cm<sup>2</sup>sec). This falls rapidly to a value of 17.5 cal/cm<sup>2</sup>sec at a distance of about 2 inches from the injector face and then remains constant for the rest of the chamber length. This pattern has been interpreted as the consequence of intense, non-equilibrium flame radiation close to the injector, followed by equilibrium gas radiation in the downstream part of the chamber.

At the higher propellant flux (6.9 g/cm<sup>2</sup>sec) the intensity pattern is somewhat different. Whilst close to the injector, the steep fall within the distance covered by the first two stations is accurately reproduced, but the intensity then rises almost as steeply within the next two stations and assumes a constant value somewhat below that of the peak value recorded close to the injector. It is believed that the extension of the high-intensity zone can be related to the displacement and increase of the flame zone at higher propellant fluxes. To verify this hypothesis, further tests with combustion chambers of increased length are in preparation.

3.2 THERMAL PROPERTIES

Thermal Conductivity Measurements on Fluids at Very High Pressures UNCLASSIFIED

A high pressure facility is being set up for measurement of the thermal conductivity of fluids at pressures up to 3000 atm and at temperatures up to 200°C. A Burckhardt oil pump supplies the working pressure which is applied to the test fluid through a mercury-filled Hart gas compressor. The pump and compressor have been installed, together with ancillary measuring and indicating equipment. The design of the high pressure autoclave and thermostat has been completed and their construction is proceeding. The

/conductivity .....

conductivity measurements will be made in a modified version of the co-axial cylinder cell used in previous work at lower pressures.

Convective Heat Transfer to Supercritical Kerosine

UNCLASSIFIED

Cine films have been taken at 5000 f.p.s. of convective heat transfer from a 1/16 inch diameter heated rod to kerosine, at supercritical pressures and under nucleate boiling conditions.

These films show that the degree of local turbulence on the heated surface is apparently similar for supercritical and boiling heat transfer, for the same values of heat flux, although in the case of supercritical pressures, considerably higher surface temperatures are attained.

The measurement of temperature and velocity distribution in the boundary layer close to the hot surface has been delayed by modifications to a differential, high-pressure, capacitance micro-manometer, to enable it to be used with a liquid flow system. Miniature velocity probes, constructed from 0.006 inch diameter stainless steel tube are available.

Internal traversing probes, designed to measure the axial variation of surface temperature, have been constructed and tested successfully, and experiments are proceeding to determine the effects of flow rate, pressure, and heat flux on this temperature distribution.

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4.1 IMPROVEMENTS TO MEET SERVICE REQUIREMENTS

Combustible Cartridge Cases

CONFIDENTIAL

Burning Rate

The results of exploratory firings in the Small Closed Vessel showed a fair degree of round to round reproducibility; test pieces prepared by sawing were found to be more consistent than stamped samples.

Nitroglycerine Absorption

A trial carried out at 120°F with case samples containing NQ propellant showed that after 140 days the nitroglycerine absorbed, 12.2 per cent, was similar to that absorbed in 14 days at 160°F. Samples fired in the Small Closed Vessel showed comparable burning rates, which were two to three times those of unstored material.

One point which these storage trials has highlighted is the severe drop in vivacity of propellant stored in the combustible case. Closed Vessel firings with the 20/1 ratio of propellant to combustible case, as would be used in the 120 mm tank gun, showed a fall in vivacity of the mixture by 6.1 per cent after 14 days at 160°F, corresponding to a velocity drop of about 145 ft/sec in the 105 mm tank gun.

Further attempts have been made to reduce the extent of the absorption of nitroglycerine by the case by enclosing the propellant in heat sealable bags. Melinex and aluminium foil barriers have considerably reduced nitroglycerine absorption and appear preferable to the methyl cellulose double dip favoured in the U.S.A. which gives only modest protection.

Alternative Binders

The Armour type process is now well established at R.O.F. Bisphampton for the manufacture of 120 mm cartridge cases. There are handling problems associated with the resin impregnation stage under production conditions, and it seemed appropriate to examine, once again, the possibility of using other materials for binding the fibre structure to form the case wall.

A number of latex dispersions based on styrene/butadiene copolymers with a high styrene content, as used in the commercial manufacture of fibre-board, are being assessed in small scale trials. The latex is present with the fibres in the felting tank; a felt is formed, dried to 6 per cent residual moisture, and given a short pressing in a hot mould to flux the polymer.

Discs 2¾ inch in diameter have been pressed between a pair of platens, one or both of which were steam heated, and samples cut from the discs for estimation of physical and burning properties. The factors investigated have included:

/(a) .....

- (a) different latex dispersions,
- (b) the latex content, from 10 to 20 per cent,
- (c) the platen temperature,
- (d) the time of pressing,
- (e) the pressure on the discs,
- (f) addition of wax to improve water resistance.

Appreciably higher tensile strengths have been obtained than are achieved with the Armour process, being about 4500 p.s.i. under the most favourable processing conditions.

Comparative water absorption tests were conducted with a composition, Pyro NC/Kraft/latex 54/27/19 and the standard Pyro NC/Kraft/Formvar 50/25/25 material.

The absorption of the latex type samples was appreciably less after 35 minutes immersion, being about  $6\frac{1}{2}$  and  $3\frac{1}{2}$  per cent for the plain and waxed samples, respectively, compared with over 20 per cent for the standard.

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HIGH EXPLOSIVES5.1 SAFETY CERTIFICATE TESTS; HAZARD APPRAISAL; AD HOC TRIALSFriction Sensitiveness

CONFIDENTIAL

The sliding block friction machine (see TR.2/63, p.29) has been used with crystalline secondary explosives, and admixture with 10 per cent Corundum (3F) gives useful results with RDX,  $\beta$  HMX, PETN and tetryl. The modifications already made have improved reproducibility, and further changes now being carried out should facilitate the preparation of the blocks and general operation of the machine. Partial ignitions only are observed, and with crystalline explosives these are shown by streaks on the blocks.

A German friction machine commercially available, and used by the Bundesanstalt für Materialprüfung (BAM) is also being evaluated. This test simulates a pestle and mortar operation at loads varying from 0.1 to 36 Kg. The same explosives as above all gave a useful range of ignitions, again only partial. Some composite propellants have also been found to respond in this test. A particular advantage is the short time required for testing, this being about 1 hour compared with 2 days with the sliding block machine.

Table 6 shows the loads giving one out of ten, and one out of six ignitions, for the sliding block and BAM machines respectively, compared with the results for the boxwood and yorkstone combination in the mallet friction test. This latter test is the nearest equivalent in our existing range of tests.

TABLE 6

Explosive	Sliding Block Load for 1/10 Ignitions	BAM Machine Load for 1/6 Ignitions	Boxwood/Yorkstone No. of Ignitions in 10 Trials
RDX	50 lb.	20 Kg	0
$\beta$ HMX	60 lb.	16.8 Kg	2
Tetryl	9 lb.	12 - 24 Kg	2
PETN	0.5 lb.	3.8 Kg	10
Barium styphnate	0.25 lb.	0.7 Kg	10
RD.2416	80 lb.	9.6 Kg	6
U.188	96 lb.	9.0 Kg	9

/It .....

It can be seen that both of the new machines span the range of the mallet test quite usefully and when further information on the effect of grit and particle size has been obtained should give better differentiation between individual explosives, and between "ignitions" and "non-ignitions". Moreover, except for the two propellants in the sliding block test, there appears to be general agreement by the three tests, i.e. the sensitive materials according to the mallet test require the smallest load in the two machine tests, and vice versa. In this connection it is interesting to note the relative velocities of movement in the three tests, i.e. 22 ft/sec in the sliding block machine, a few ft/sec in the BAM machine, and 50 - 60 ft/sec in the mallet test.

The two propellants were tested as a thin sliver, and it is thought that this accounts for the difference in the results between the sliding block on the one hand, and the BAM and mallet test on the other. In the latter two cases the upper frictional surface grinds through the sliver, and the propellant is in more intimate contact with the two surfaces. In the sliding block case, even though corundum was placed on both sides of the sliver, no such intimate grinding through takes place. Consequently the load for ignition is apparently much larger.

Too much weight should not be attached to the sliding block figure for barium styphnate, since all materials more sensitive than PETN in the presence of grit will give figures in the range 0 to 0.5 lb. load.

### 5.3 FUNCTIONING AND DETONATION STUDIES

#### Measurement of the Temperature of the Detonation Front in Condensed Explosives

UNCLASSIFIED

As forecast in TR.2/63 the use of reflective optics has greatly reduced the scatter and it has been possible to determine the detonation temperatures and emissivities of nitromethane, ethyl nitrate and diethylene glycol dinitrate with precision. The work has been reported (Nature, 202, 758) and the results obtained are summarised as follows:

TABLE 7

Explosive	No. of Determinations	Emissivity	Detonation Temperature
Nitromethane	15	1.15	$3380 \pm 20^{\circ}\text{K}$
Ethyl nitrate	6	1.15	$3130 \pm 20^{\circ}\text{K}$
DEGN	6	1.20	$3320 \pm 20^{\circ}\text{K}$

/There .....



There are no other published values for the detonation temperatures of DEGN or ethyl nitrate. The value for nitromethane is identical with that obtained in unpublished work at Los Alamos, but less than other published experimental values (3700°K, 3800°K). Various theoretical values have been derived using Kistiakowsky/Wilson and Lennard-Jones/Devonshire equations of state but these are lower than the experimental value of 3380°K, indicating that repulsion forces have been over-estimated.

The spectral distribution of visible radiation from the detonation products of several explosives has been shown from previous work to be grey body in nature, but without the present precision it was impossible to ascribe values to the product emissivities. It is now apparent that the emissivities of the above explosive products are similar and very close to that of a black body. This fact might have been predicted from statistical and quantum mechanical considerations, but there is a possibility that it is associated with the formation of free carbon in the products of these fuel-rich explosives. To test this point, similar measurements will be made on both oxygen-balanced and carbon-free explosives.

#### Theory of Shock Initiation

UNCLASSIFIED

The conditions under which the particle velocity gradient in a reactive shock wave can be a function of time only have been examined by an analytical method. Exact solutions for the development of a strong shock can be obtained if the rate of change of pressure due to chemical reaction is itself a function of time. The required functions are derived by an inverse method in terms of the polytropic exponent  $\gamma = (\partial \ln p / \partial \ln \rho)_s$  and an arbitrary constant which determines the sense of the pressure gradient behind the shock front. Where this is zero, corresponding to a step shock, the volumetric reaction rate can be expressed as a function of pressure. Exact solutions with a time-dependent velocity gradient are found to be possible only when the exponent of pressure is less than unity and a particular function of  $\gamma$ .

The results are being used to examine the validity of various approximate methods of obtaining solutions to reactive shock problems.

#### The Simulation of Aircraft Sonic Bangs by Explosives

RESTRICTED

The increasing use of supersonic aircraft emphasises the problem of assessing the effects of sonic bangs on people and structures. The use of supersonic aircraft for an investigation of this type is very expensive and explosives were suggested as an alternative method of producing sonic bang waveforms. The required waveform is that of a classical N-wave, with overpressures in the range 1 lb/ft<sup>2</sup> to 2 lb/ft<sup>2</sup> and a duration of between 100 milliseconds and 300 milliseconds.

To produce the required N-wave with normal, that is, point source explosive charges would necessitate impossibly large charges at great distances. However, a new technique is being developed in which linear explosive charges weighing only a few pounds are detonated at a distance of about 100 yards. The shape of the waveform reaching the observer depends on the angle between the observer and the direction the linear charge is pointing, but for angles up to about 45° the waveforms produced to date are promising.

/A length .....



A length of Cordtex detonating cord is equivalent to a linear array of point sources of explosive, each of low effective weight. At a distance of 100 yards from the charge the shock waves produced in the air are so weak that they may be regarded as practically isentropic and the pressure pulse from each consecutive point source as additive to that of its predecessor and successor. The result for a simple linear charge viewed end-on is that the positive and negative pressure phases for each point cancel out except for the ends of the charge. By placing strands of different lengths in parallel it is possible to tailor the waveform to a close approximation to the required shape.

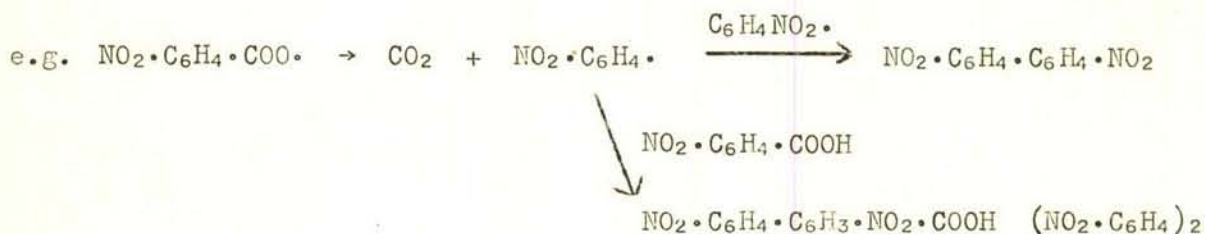
There is, however, an associated "noise" having indeterminate frequency components and amplitude similar to that of the N-wave. This "noise" is more noticeable in air bursts carried out by suspending the linear charges from barrage balloons than in firings close to ground level and its origin is as yet unknown. All waveforms and "noise" are monitored using a calibrated H3 piezoelectric gauge with its associated amplifiers and display equipment. At trials carried out in collaboration with R.A.E. Farnborough similar records were obtained using condenser microphone gauges. Further attempts will be made to produce N-waves free from the unwanted frequencies by firing charges in proximity to the ground.

## Thermal Decomposition of Solids

## Peracids

UNCLASSIFIED

The mechanism of the thermal decomposition of substituted peroxybenzoic acids has been outlined previously (TR.1/63, p.33). With p-nitro-peroxybenzoic acid, the decomposition takes place on the solid surface where the p-nitrobenzoyloxy radicals formed are firmly held; thus their direct interaction is prevented and p-nitrobenzoic acid is virtually the only solid product. During the decomposition of m-nitroperoxybenzoic acid, however, melting occurs; the radicals formed are therefore more mobile and the eventual product, mainly m-nitrobenzoic acid, contains about 1 per cent impurity. By means of thin layer chromatography using an alumina stationary phase, a 40 per cent  $\text{CCl}_4$ : 10 per cent  $\text{CHCl}_3$ : 58 per cent  $\text{C}_6\text{H}_5\text{CH}_3$  mobile phase, and developing the plates with titanous chloride and dimethylaminobenzaldehyde, four impurity spots have been obtained: each is a nitro compound. Very small quantities of each have been isolated using a 1 mm-thick plate. Examination of these on the mass spectrometer has shown that three of the compounds are dinitrodiphenyl derivatives. The  $R_F$  values of 2,2', 2,3' and 3,3'-dinitrodiphenyl, synthesised from the appropriate bromonitrobenzenes by the Ullman reaction, confirm their presence. Clearly these compounds are formed by minor secondary reaction of m-nitrobenzoyloxy radicals,



/When . . . .



When a mixture of m-nitroperoxybenzoic acid and p-nitroperoxybenzoic acid is decomposed at 79°C, six impurities have been detected including 3,4' and 4,4'-dinitrodiphenyl. The decomposition of p-nitroperoxybenzoic acid at this temperature under these conditions is of interest with regard to the role of intermolecular forces.

p-Chloroperoxybenzoic acid (m.p. 103°C) has been prepared from p-chlorobenzoyl peroxide by a modified Braun synthesis and its decomposition studied at 86° and 92°C. The process is similar to that for p-nitroperoxybenzoic acid, the products being p-chlorobenzoic acid, carbon dioxide, water and hydrogen chloride.

Nitramines

UNCLASSIFIED

An investigation into the thermal decomposition of RDX has begun, and preliminary experiments carried out in order to obtain a quantity of partially decomposed material confirms the occurrence of an abrupt change in the rate of gas evolution when the material melts. Evidence of two distinct impurities in the partly decomposed material has been obtained by thin layer chromatography but these materials have not yet been isolated and identified. U.V. examination of an acetone solution of the residue indicates an impurity band at 327 mμ.

5.4 COMPOSITE H.E.

Tests of Processing Equipment for High Energy Compositions

RESTRICTED

In the course of the development of equipment to process high energy compositions a number of ad hoc explosives safety trials are necessary. Two of these carried out in the period under review have been concerned with an outlet valve for a mixing pot in one trial and a pair of curing ovens in the other.

The outlet valve was built into a dummy mixing pot assembly and, after some preliminary trials with inert materials, operated whilst flooded with neat nitroglycerine at 10 cycles per minute for over 1000 cycles without incident.

The curing ovens for this work will be enclosed in a form of mounding based on spun concrete pipe. The ovens are arranged in pairs and designed so as to limit blast in one direction by means of explosion-proof doors. The object of the trial was to test the design of these doors and to test the possibility of the detonation of a full charge (2 lb.) in one oven causing a sympathetic detonation in the other. A dummy mould filled with 2 lb. of P.E. 3A was detonated in one oven whilst in the other a small polished brass witness device supported two small heaps of lead azide.

Blastmeters showed that the blast had been controlled and the brass witness indicated sympathetic detonation had not occurred with the lead azide, but the heavy steel door was blown clear through its frame and a stronger version is being designed.

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6

INITIATING EXPLOSIVES AND IGNIFEROUS COMPOSITIONS

6.1 NEW OR IMPROVED COMPOSITIONS

Lead Trinitrophloroglucinate

RESTRICTED

Seven lead compounds of trinitrophloroglucinol have now been isolated and identified from the interaction of soluble lead salts and magnesium trinitrophloroglucinate solution. Two are hydrates, and the main interest still centres on the free-flowing composition R.D.1359; this has now been tested by R.A.R.D.E. and is recommended for Ordnance Board trials in Fuze 947, which is expected to be adopted for nearly all aircraft bomb detonators. In the preparation of R.D.1359 it is essential for the pentahydrate intermediate to be completely converted, as this substance has been isolated and shown to decompose with explosive violence at 150°C, a temperature much lower than that required to decompose the anhydrous Types A and B.

Compositions for Thermal and Electrically Initiated Stores    CONFIDENTIAL

Monopotassium 4:6 dinitroresorcinate has been made in the form of compact free-flowing crystals in a preparation scaled up to ¾ lb. batch. Although much less sensitive mechanically than the lead salts (R.D.1308 and R.D.1353) with F.I. = 60 and no ignitions by friction wood on wood or at 12 ft/sec pendulum friction machine, it will ignite reliably from a bridgewire with a current of 0.8 amp at 12 volts, and by the standard pulse employed for I.C.I. capsule firing. Tests in these capsules at Ardeer have shown that it will ignite the standard 2 second delay composition. Other potassium salts, e.g. of picric acid, 3:5 dinitrocatechol, dinitro-ortho-cresol, and trinitrophloroglucinol, are also being examined because of their satisfactory stability at 170°C.

Detonators Using Secondary Explosives

CONFIDENTIAL

Both PETN and RDX have been prepared in ranges of particle sizes and of modified crystal habit for tests as described in A.R.D.E.(MX) 34/61. The Service requirement is now concentrated upon RDX because of its better thermal stability and lower mechanical sensitiveness. The objective is to achieve reliable functioning in the wire bridge detonator with 1 Kv and 0.3 Mfd condenser. American work showed that RDX of acicular crystal habit responded to lower energies; this has been confirmed and extended because it seemed likely that dendritic rather than acicular habit should provide a more consistent air/explosive ratio. Dendritic RDX has been prepared by a simple process using acetone as solvent and preliminary tests in the detonator have given sensitivity significantly greater than any RDX tested previously; dendritic RDX containing co-precipitated semi-colloidal graphite was less sensitive.

Tribasic Lead Styphnate

RESTRICTED

The preparation and properties of this substance are being studied with a view to providing a less brisant and slower burning composition for explosive motor and igniter requirements and an ingredient to replace normal lead styphnate/lead dioxide mixtures in cap compositions. The literature refers

/to .....



to preparation by digesting normal lead styphnate with litharge in water at 90°C for three hours. By the interaction of solutions two distinctive and reproducible products have been isolated with lead contents of 72.5 per cent and 78.7 per cent.

The properties are somewhat unexpected and interesting. There is no decomposition after 4 hours heating at 135°C and ignition temperature is 238°C. Sensitiveness to electrostatic spark ignition and to friction are greater than for normal lead styphnate (R.D.1303M). Nevertheless the violence on ignition is much reduced as shown by tests in I.C.I. nylon capsules. It will propagate satisfactorily as a component (80/20) of conducting composition in N8 igniter giving only a weak flame. When co-precipitated with 12.6 per cent boron it has very good igniting properties without violence. This unusual combination of properties promise technical applications in C.C. igniters, bridgewire type capsules and delay systems.

Primary Explosives: Developments in Australia

RESTRICTED

At the request of the Senior Representative in London of the Department of Supply a visit has been made to Australia to advise on the manufacture of initiating compositions originated in E.R.D.E., to inspect processes on site, and to discuss current problems and research. Eight establishments were visited, including the main filling factory at St. Marys (where nine E.R.D.E. compositions are manufactured), the Directorate of Inspection and Defence Standards Laboratory. Useful discussions took place covering research and development of primary explosives, igniferous compositions and elastic pyrotechnics and manufacturing safety. A brief visit was included to Messrs. I.C.I.A.N.Z. where initiator manufacturing plant was seen and Ministry of Aviation developments of possible commercial interest discussed.

Pyrotechnic and Igniter Compositions

RESTRICTED

Reports have been completed describing the development and methods of preparation of elastic pyrotechnics for priming applications, signal cartridges, tracking flares, smoke compositions, and the development and manufacture of R.I.10 composition for 2-inch air-to-air rockets.

6.2 STUDIES OF BEHAVIOUR

Photoconductivity of Lead Azide

UNCLASSIFIED

Using specially prepared crystals of alpha lead azide, measurements in the wavelength range 3500 Å to 6500 Å were made at various temperatures between 20°C and -196°C. In the curves of photocurrent versus wavelength, a broad peak is centred around 4800 Å, and a much sharper, higher peak at 4050 Å. The photocurrent at the latter wavelength showed markedly greater temperature dependence than elsewhere, corresponding to an activation energy of 8.2 kcal in the range 20°C down to -50°C. At all other wavelengths, including 4800 Å, the activation energy over the whole temperature-range was 0.8 kcal, a value which also applied below -50°C to the photocurrent at 4050 Å.

/It .....



It has also been found that the photocurrent is, at all wavelengths, proportional to the square root of the light intensity. This is contrary to the results quoted in TR.2/63, but it indicates a second-order termination process more in keeping with expectation (recombination of an electron and a positive hole). Attributing the 4050 Å peak to the promotion of an electron from the valence band to the main exciton level, the 8.2 kcal activation energy is that required to decompose the exciton thermally and release an electron to the conduction band. Provisionally, the 0.8 kcal activation energy associated with all other wavelengths is indicative of a pre-dissociation level closer to the conduction band, and it appears that promotion to this level takes place from a wide range of (minor) impurity levels.

In order to interpret the energy levels more definitely, the above thermal gap (8.2 kcal) between exciton level and conduction band needs to be combined with the ratio of dielectric constants at low and high frequencies. Low-frequency measurement is being attempted by matching known capacitances against cells containing crystals of lead azide immersed in liquids of known dielectric constant.

#### The Refractive Indices of Alkali Azides

UNCLASSIFIED

The refractive indices of sodium, potassium, rubidium and caesium azides have been measured along their main crystallographic axes. In each case a modification of Bragg's method has enabled the atomic refractivity of the nitrogens of the azide ion to be calculated, and the position of the dipoles created by electron polarisation established. Table 8 shows these figures, together with corresponding values for silver azide calculated from literature values for two of its three indices.

TABLE 8

	NaN <sub>3</sub>	KN <sub>3</sub>	RbN <sub>3</sub>	CsN <sub>3</sub>	AgN <sub>3</sub>
Nitrogen refractivity	4.4	5.25	5.40	5.50	5.00
Distance of dipoles from central nitrogen	0.95 Å	0.85 Å	0.88 Å	0.89 Å	0.89 Å

The distance of 0.95 Å for NaN<sub>3</sub> may be explained in terms of the relative positions of the azide and sodium ions in the rhombohedral lattice. The trend in nitrogen refractivity is also to be expected in view of the lower inductive effect of the ions of higher atomic weight. Our aim is to relate these refractivities to the activation energy of thermal decomposition. We have studied sodium azide and obtained a value of 33 kcal/mole for both the induction period and main reaction. Literature values for KN<sub>3</sub> and AgN<sub>3</sub> are 49 kcal/mole and 44 kcal/mole respectively. The position of silver azide between sodium and potassium azides for both nitrogen refractivity and activation energy is interesting.

/Double .....



Double Azides of Barium and Caesium

UNCLASSIFIED

During the recrystallisation of caesium azide from water, distinct double salts giving new X-ray diffraction patterns and analysing as  $\text{CsN}_3 \cdot 2\text{BaN}_6$  and  $2\text{CsN}_3 \cdot \text{BaN}_6$  were obtained. Such double azides have not been reported before and offer interesting possibilities for studying decomposition behaviour. If decomposition involves the promotion of an electron into an excited level associated with the lattice as a whole, the decomposition will be different from that of either of the constituent salts; if the electron transfer is to the nearest neighbour only, then decomposition behaviour is likely to follow that of  $\text{CsN}_3$  and  $\text{BaN}_6$  and may take place in two stages. More of these double salts are being prepared.

/7 .....

7

NON-METALLIC MATERIALS

7.1 POLYMERIC TYPES

7.1.2 Thermoplastics

Sound Velocity Method of Measuring the Bulk Modulus of Elasticity of a Polymer

UNCLASSIFIED

The ultrasonic interferometer has been used to measure the velocity of sound, at 1.45 Mc/sec and 20°C, in small disc samples of polyethylene having the following densities, 0.920, 0.938, 0.951, 0.953, 0.955, 0.963 gm/cc. A plot of sound velocity versus density does not conclusively show that the relationship is linear or cubic. This recent work has been submitted for publication in the "Journal of Polymer Science" and the earlier report describing the apparatus used has been accepted for publication in "Polymer".

The velocities are converted to dynamic Young's moduli using Poisson's ratios given by Schuyer (1959). Comparison of these results with the lower frequency moduli of Davidse, Waterman and Westerdyke indicate that the test conditions may well be close to those pertaining when viscoelastic effects have been eliminated. The bulk moduli B obtained from the velocities is found to follow the equation  $B = B_A (d_c - d_a) / (d_c - d)$  where  $B_A$  is a constant and d the density of the test material. The quantities  $d_c$  and  $d_a$  are the densities of the crystalline and amorphous regions respectively. This equation is now the subject of theoretical study.

Impact Experiments on Polymers

UNCLASSIFIED

It has been shown that the experiments on the longitudinal impact of a steel sphere on the flat end of a cylindrical rod provide an experimental means of studying the combined elastic and plastic properties of a material. Thus it is possible to determine the engineering limits of a material under compression. So far our investigations in this direction have included a detailed study for mild steel and preliminary measurements for Perspex.

Elastic Modulus of Polymers from Resonant Flexure of Clamped Discs

UNCLASSIFIED

Development work has continued on the electrostatic technique which utilizes the electrostatic charge on the surface of a polymer to detect the vibrations of a centrally clamped disc in forced vibration. An advantage of the technique is that it measures velocity resonance, and hence the natural frequency from which flexural modulus is calculated. Values of specific loss are obtained by extending the method to measure the phase difference between the applied force and the deformation.

/The .....



The development of the method of test and the results published to date ("Journal of Scientific Instruments, Vol. 41 June 1964") are for experiments in which thin discs vibrate with a single nodal diameter at room temperature. The polymers tested are poly(methyl methacrylate) and four grades of polyethylene.

A recent form of the apparatus using a new method to excite the discs into vibration has been used to study the dynamic mechanical properties of high modulus reinforced materials. A further new aspect now being pursued is the measurement of the dynamic Poisson's ratio which is an essential element in the design of many engineering structures.

Contact Electrification

UNCLASSIFIED

The contact electrification experiments have resulted in the development of a simple pressure sensitive unit which could be calibrated to provide a simple technique for the determination of pressure and wave shape in detonation waves. This transducer unit consists of two polymer plates between which is sandwiched a spiral of wire. The spiral is connected to earth through a high resistance across which there is a voltage detector, e.g. an oscilloscope. It is this voltage generated across the resistance which is calibrated against pressure on the unit. Preliminary gauges use polymer plates of Perspex one inch square and 3/8 inch thick.

7.1.3 Rubbers

Dynamic Properties of Rubbers and Plastics:  
E.M.R. Contract with R.A.P.R.A.

UNCLASSIFIED

Information is required by F.V.R.D.E. with regard to the abrasive wear of various rubbers as tank track pads at running temperatures. The approximate working temperature reached by three rubbers after 2 hours running in this country was: natural rubber, 50°C; butadiene-styrene rubber, 75°C; and polyurethane, 90°C.

A programme is being prepared to compare the abrasion resistance and tear resistance of polyester-urethanes and polyether-urethanes with those of a standard natural rubber compound at high temperatures.

Permeability of Elastomers to Organic Liquids

UNCLASSIFIED

The scatter of results previously reported was reduced by stricter control of temperature and air-flow over the exposed surface of the test specimen.

Tests carried out using iso-octane and toluene suggest that if the permeability of polyethylene film to each solvent is measured, then that for a mixture of these solvents can be calculated.

/Aging .....



Aging Trials on Rubbers

UNCLASSIFIED

The trials on nitrile rubber, neoprene WRT, neoprene ILA, polyester-urethane, polyether-urethane and a PVC/nitrile rubber blend under hot-dry, hot-wet immersion and hot-humid conditions all at 70°C are continuing. After 24 weeks at 70°C the nitrile and neoprene WRT rubbers in the dry condition are showing only a slight decrease in elongation at break; for the other conditions there is little change (e.g. when immersed in water or subjected to 100 per cent relative humidity). The neoprene ILA when immersed in water shows a decrease in tensile strength and elongation at break and only slight changes under dry conditions and at 100 per cent relative humidity. The polyester-urethane decreased in tensile strength in the dry conditions by over 90 per cent. In addition previous results showed that this material had lost all its physical properties after 2 weeks immersion in water and also at 100 per cent humidity.

After 2 weeks in hot-humid conditions (70°C and 100 per cent r.h.) the polyether-urethane showed a 50 per cent reduction in original tensile strength. Similar results were obtained when immersed in water at that temperature. After 4 weeks in dry air there was only a 25 per cent loss of tensile strength. The elongation at break of the polyether-urethanes have risen slightly in all cases.

Test sheets of all the rubbers are being prepared for exposure at the Tropical Research Unit in Australia.

Compatibility of Rubber with Explosives

UNCLASSIFIED

Vulcanizates of ethylene/propylene terpolymer, fluorinated copolymer and neoprene ILA have been prepared and are being tested for compatibility with explosives.

Polyurethanes: Rubbers for Aging Studies

UNCLASSIFIED

The preparation of polyesters has been resumed. The polyesters produced will be used for the preparation of polyester polyurethane rubbers, and for adhesives. The polyurethane rubbers are required for part of a J.T.R.U. programme, and also for use in a new laboratory programme on the degradation of rubbers under the influence of heat, air and moisture. One polyurethane rubber produced in this work is to be examined as a possible thread sealing compound.

7.1.4 General Polymer Investigations

Degradation of Polymers

UNCLASSIFIED

The effects of (electron) radiation dose and molecular weight on the tensile and flexural properties of polycarbonate have been examined in detail. Tensile strength, flexural strength and flexural modulus can be expressed as linear functions of molecular weight when the material is ductile. The strength of the brittle material (molecular weights less than 13,000), however, has been shown to be a linear function of reciprocal molecular weight. The effect of molecular weight on flexural modulus has also been examined.

/The .....



The presence of the equilibrium water content in the plastic has been shown to cause a four-fold increase in the rate of chain scission, an effect which can be explained on the basis of the mechanism of degradation previously advanced.

This work has been accepted for publication in the J. Polymer Science.

The thermal degradation of polycarbonate is being further examined. It has been found that the behaviour of this polymer is very dependent on the conditions of degradation. Thus, when it is heated and evacuated continuously it crosslinks, whereas, when heated in a sealed evacuated tube it undergoes chain scission (E.R.D.E. TR.2/63). The kinetics of gel formation in the open evacuated system are being examined. It has also been observed that in both open and closed evacuated systems a colour is developed during degradation which is similar to that formed during electron irradiation. The nature of the colour and the kinetics of its formation are being examined.

Polycarbonate synthesised by the Chemical Engineering Branch and known to be free from possible additives (e.g. anti-oxidants, etc.) is now being used in these studies to eliminate this unknown factor involved in the use of commercial material.

A study of the viscosity of electron irradiated polytetramethylene oxide specimens showed that the 'weak links' observed during thermal degradation studies were rapidly and preferentially destroyed by irradiation. Analysis of the solubility behaviour of the polymer after destruction of the weak links indicated a subsequent ratio of main chain scissions to cross links of 0.37. These changes were accompanied by the evolution of hydrogen,  $G(H_2) = 0.8$ , and traces of other gases. The results of both the thermal and irradiation studies of polytetramethylene oxide have been accepted for publication in Makromol. Chemie.

#### Preparation of Polycarbonate

UNCLASSIFIED

In purifying bisphenol A for the preparation of polycarbonate, two recrystallisations from toluene gave as pure a product (free from possible degradation catalysts) as was given by other methods, and this treatment was adopted. Polycarbonate is made by bubbling phosgene through a mixture of aqueous alkaline bisphenol and catalyst, and methylene chloride solvent, at 20°C. The solvent layer, which dissolves the polycarbonate product, is then separated, washed with water and the product extracted from it. Three 50-gram trial preparations were made, and it was found that the molecular weight of the product could be regulated according to the reaction time given. Finally 1000 grams of product of molecular weight 25,000 grams and 500 grams of molecular weight 75,000 grams were made. Extraction of the product gave a sticky intractable material, and will merit development if larger quantities are required.

/Stress-Cracking .....



Stress-Cracking of Polymers

UNCLASSIFIED

Work is being done for the I.S.O. Plastics Committee (ISO/TC/61/WG-6) on the stress-cracking of low density polyethylene. Sheets are being moulded under specified conditions and test-pieces with a controlled cut in them will be immersed under strain in solvent (Igepal 630) and the total number of failures by cracking in 48 hours will be recorded.

Aging of Polyacetals

UNCLASSIFIED

It was indicated in previous tests that polyacetals, in the form of components prepared by manufacturers and test-pieces prepared in these laboratories, broke down in hot-humid conditions. Also it was found that the homopolymer decomposes at a different rate to the copolymer.

A programme of work has been started to compare the rates of decomposition, as measured by the physical properties, of three commercially available polyacetals (1 homopolymer and 2 copolymers).

Test-pieces are being prepared for exposure tests at the Tropical Research Unit in Australia.

Nylon Spacer Pieces in Hydraulic Fluid (OF24)

UNCLASSIFIED

It has been suggested that a nylon spacer piece should replace a metal one in the braking system of a transport vehicle. Tests have been carried out on test-pieces prepared at E.R.D.E. (Nylon 66 and Nylon 11) and on the spacer pieces (Nylon 11) supplied by F.V.R.D.E. The materials have been immersed in hydraulic fluid, OF24, at 70°C and after two months immersion there is little change.

Autoxidation of Polymers

RESTRICTED

The study of the previously described model substances for polyolefin and polyamide autoxidation has been continued: the range was extended by adopting N-pentylhexanamide as a model substance for nylon. The testing of antioxidant activity with the recording Martin apparatus was concentrated mainly on 2,6,10,14-tetramethylpentadecane and N-pentylhexanamide in the temperature range 120 - 140°C and it was found that with these model substances too, some of the newly developed antioxidants such as 6-t-butyl, 3,7,8,2'5'-pentahydroxyflavone and 3',4',5'-trihydroxy-4''-t-butylpolyporic acid compared favourably with those in commercial use.

The conversion of metal catalyst at high concentrations into inhibitors, previously found to occur with alk-1-enes, 2,6,10,14-tetramethylpentadecane and cobalt (II) catalyst, was also demonstrated in the following systems: methyl linoleate and bis(N-butyl salicylaldimino) cobalt (II); N-butyl acetamide and tris(N-butyl salicylaldimino) cobalt (III); N-butyl acetamide and cobaltous acetate. This newly discovered phenomenon in the field of metal catalyzed autoxidation is frequently undetectable because of the solubility limitations e.g. in the case of N-pentylhexanamide and cobaltous acetate where the solubility of the catalyst is limited to approximately M/4000. This is substantially below the concentration at which the maximum catalytic activity of cobaltous acetate, as measured by the length of the induction period, was observed in other model amides which was approximately M/1000.

/The .....



The study of gamma-ray induced autoxidation in the solid state was extended from docos-1-ene to other alk-1-enes, particularly eicos-1-ene, and quantitative data were obtained on the effect of dose rate, oxygen partial pressure and surface area.

Ferric acetylacetonate was found to be a photo-sensitiser in the autoxidation of N-pentylhexanamide (at 365 mμ). Concentration effects and other kinetic features were examined and it was found that the catalytic activity of the photo-catalyst could be inhibited by the addition of inorganic fluorides particularly caesium fluoride. The latter was found to be soluble in N-pentylhexanamide to an extent of  $1.7 \times 10^{-3}$  M; presumably solubility in nylon would be of a similar order of magnitude. Moreover, the photo-sensitised autoxidation of pure N-pentylhexanamide was inhibited by caesium fluoride when light of wavelength >350 mμ was used. Since N-pentylhexanamide does not measurably absorb light in this range of the spectrum, it is postulated that the photosensitized autoxidation is due to trace metals, particularly iron, the photocatalytic effect of which is inhibited by fluorides. In view of the likelihood that this method could be applied in the stabilisation of polymers against photo-sensitised degradation, work has now been started with a view to applying the positive results achieved with model substances to nylon and other polymers.

Heat-Resistant Materials: Silicon-Nitrogen Polymers, etc:

E.M.R. Contract with Westfield College

UNCLASSIFIED

Silyl piperidine has been synthesised and some of its physical properties determined, e.g. vapour pressure, infra-red spectrum, molecular weight and density. The reactivity of the silyl group in this molecule is being investigated prior to the synthesis of di-silyl-piperazine, which should be a useful difunctional polymerisation intermediate.

Yields of  $(\text{SiF}_3)_2\text{NMe}$ , the monomer used to prepare fluorinated silicon-nitrogen polymers, have been increased from 5 - 10 per cent to 20 per cent by using diborane instead of lithium aluminium hydride to remove HF eliminated in the reaction between  $\text{SiF}_4$  and  $\text{MeNH}_2$ .

Heat-Resistant Materials: Oligomeric and Polymeric Compounds Based on Phosphorus, Arsenic, Antimony, Bismuth, etc:

E.M.R. Contract with Birkbeck College

UNCLASSIFIED

Further boron-phosphorus molecular addition compounds have been synthesised in order to investigate whether they can be converted into cyclic phosphinoborines. One of these,  $\text{Ph}_2\text{PHBPh}_2\text{I}$ , gave a stable inert material of composition  $\text{Ph}_2\text{PBPh}_2$ , but another,  $\text{Ph}_2\text{PHBCl}_3$ , did not undergo dehydrohalogenation.

Work on the selective halogenation of inorganic hydrides by means of N-halogeno-succinimide has continued; tri-aryl and tri-alkyl-silanes and germanes have been brominated and both mono- and di-bromo derivatives have been obtained from cyclotriphosphenoborines.

/Heat-Resistant .....



Heat-Resistant Polymers - Polybenzimidazoles

UNCLASSIFIED

Little further work has been carried out, due to the non-availability in this country of the raw material, 3,3'-diaminobenzidine. One potentially useful thermosetting resin has been prepared, but the materials examined to date show little promise as high-temperature adhesives. In the coming period, work will be concentrated on the polypyromellitimides. These are expected to be more tractable than the polybenzimidazoles in the uncured state, and raw materials for their preparation are comparatively readily available.

Polyamides - Kinetic Studies

UNCLASSIFIED

The kinetic and equilibrium studies on the system caprolactam/hexa-methylene diamine/polycapramide have been completed. The equilibrium study has been written up, and awaits publication as E.R.D.E. Report No. 8/R/64. The kinetic study is being written up for open publication.

Physical Properties and Polymer Structure

UNCLASSIFIED

Measurements of the coefficient of compressibility and expansion for crystallisable materials, hence the thermal pressure coefficient, have continued during the period. Substances examined were n-Eicosane, Dotriacontane and polytetramethylene glycol. The measurements were carried out both for the crystalline and liquid phases and the results obtained were approximately what would be expected from the chemical structure of the materials.

Difficulties have been experienced in vapour pressure measurements because of condensation of vapour in the manometer during the cooling cycle. These have been overcome by the use of a modified vapour pressure manometer operated by mercury cut-off valves which allow vapour to be pumped away during the cooling cycle. The new apparatus has the advantage that errors associated with the slow de-gassing of the mercury can be avoided.

Polymeric Organic Semi-Conductors:

E.M.R. Contract with Nottingham University

UNCLASSIFIED

The electrical properties of a series of substituted styrene homopolymers and copolymers have been investigated. The polymers had lower energy gaps for electrical conduction than pure polystyrene and the degree to which the energy gap was lower was in proportion to the polarity of the substituent. In the case of the copolymers it was hoped that adjacent donor and acceptor groups in a polymer would lower the energy gap for conduction; only one of the prepared copolymers exhibited a lower energy gap than its corresponding homopolymers, namely that of p-chloro and p-methoxystyrene. Presumably charge transfer in the other copolymers did not occur for steric reasons.

/Polyacrylonitrile .....



Polyacrylonitrile Materials for Driving Bands

RESTRICTED

A continuous impregnation apparatus has been made and used to prepare a considerable stock of test pieces and moulded-to-shape 40-mm bands from Courtelles yarn by the N,N'-formdimethylamide process. These mouldings are being stored in laboratory conditions, under vacuum at room temperature and in an air stream at 40°C, to establish whether the increase in strength, previously noted on prolonged storage in the laboratory, can be achieved more rapidly by these methods. After three months' storage, no significant increase in rate of strengthening appears to have been achieved by either method. It seems likely that diffusion of solvent within the polymer mass, rather than loss of solvent from the surface, is the rate-determining factor in the strengthening process.

Application is being made for a provisional patent on the process for obtaining strong integral mouldings from acrylonitrile copolymer fibres by compressing when partially swollen by a solvent.

Solvents other than N,N'-formdimethylamide are now being examined as swelling agents.

Polymers under High Speed Stressing

UNCLASSIFIED

Some modifications to the pendulum impact machine head are being made to facilitate strain measurement by high-speed photography. The general strain behaviour in dumb-bell specimens having an increased (3") test length is being studied with particular reference to the velocity of propagation of "plastic" strain. Initial results for "Delrin", chosen for availability and comparative ease of machining to shape, are being analysed, and dumb-bells of other thermoplastics are being obtained.

The method by which fracture energy is calculated for the fly-wheel tensile machine has been carefully re-examined subsequent to comments arising from the S.C.I. Symposium paper in which the normally used method was outlined. Various aspects of the mechanics of impact, from which energy bases in the system may be assessed, have been considered. In general, the normally used method can be justified, although the complexity of the impact process makes a complete analysis difficult.

An assessment of the limitations on maximum stressing and straining rates imposed by the Baldwin machine with its ancilliary measuring and recording equipment has been made.

A report has been prepared which relates the fracture energy with molecular weight and maximum yield strength with density for a range of high density polyethylenes. Details of methods of preparation of compression moulded sheets and dumb-bell test-pieces are given.

The report on the flexural and tensile properties of a polycarbonate degraded by electron radiation has been accepted for publication by the Journal of Polymer Science.

/Effect .....



Effect of Environment on the Delayed Rupture of  
Polymer Filaments

UNCLASSIFIED

Determinations of stress life of nylon monofilaments in darkness at 30°C have been extended from the vacuum environment to those of dry air and dry nitrogen and to some four decades of time. No significant effect of environment has been detected under these conditions.

Permeability of Polymer Films - Polymethyl Methacrylate:  
E.M.R. with Imperial College of Science and Technology,  
London

UNCLASSIFIED

Further studies of the diffusion of water in polymethyl methacrylate have been carried out. This material is a glassy polymer and may therefore have cavities in which the penetrant molecules might cluster without disturbance of the polymer matrix. It has polar groups which may increase the sorption capacity and act as centres of nucleation. High sorption in turn could lead to plasticization which would tend to increase the diffusion coefficient at a particular concentration, and this effect would be more marked as concentration increased. To find out how these features affect the diffusion process, the system has been studied at 30°, 50° and 70°C using the steady-state method. It has been shown that the sorption isotherms are independent of temperature and this is thought to indicate athermal dilution of water, due probably to the presence of gaps in the polymer matrix. The temperature coefficient of the permeability constant is zero and permeability rate is proportional to the pressure difference and is independent of temperature in the range studied.

7.2 ADHESIVES AND SEALANTS

Torsional Shear of Annular Joints

UNCLASSIFIED

A paper on this subject has been drafted and will be submitted to the 'British Journal of Applied Physics'. A letter to 'Nature' about the effect of strain rate on joint strength has been published.

Provision of equipment, designed to record loads at high strain-rates, which will be fitted to the Baldwin testing machine, is being considered as a matter of urgency.

Sealing Threaded Joints

UNCLASSIFIED

A paper (No. A.3) on "Commercial Sealants for Parallel Threaded Joints" was presented to the Second International Conference on Fluid Sealing, convened by the British Hydromechanics Research Association in April, 1964. The paper was in two parts (i) temporary seals (lutings, p.t.f.e. tapes and cord) and (ii) permanent seals (cements).

The work on cements has led to better definition of the previously stated requirements that "the set cement should be flexible ....., reasonably adherent ....., and adequately strong". If the radial strain imposed on a joint between dissimilar metals by thermal

/cycling .....



cycling is considered, the following relationship is found, assuming Hookean behaviour:

$$\sigma_r = \Delta\alpha \Delta T r E/t$$

where  $\sigma_r$  (p.s.i.) is the radial stress in the joint,  $E$  (p.s.i.) is Young's modulus,  $\Delta\alpha$  (inch/inch/°C) is the difference in coefficients of thermal expansion of the two metals,  $\Delta T$  (°C) is the change in temperature,  $r$  (inch) is the effective radius of the thread and  $t$  (inch) is the thickness of the cement layer. If  $\sigma_r$  exceeds the strength of the cement or of the joint (whichever is the less) there will result either a cohesive or adhesive failure, with leakage through the seal. Substitution in the equation of the appropriate values leads to the following requirements for a cement to maintain sealing on our thermal cycling trial.

The setting cement must at all times have a cohesive strength, and adhesive strengths with the appropriate adherends, all not less than one-tenth of its concurrent Young's modulus.

Of the nineteen cements, having a wide range of physical properties, so far examined, six (all rubbers) comply with these requirements, and these do not leak during thermal cycling. Three cements initially comply, but harden during the test and, in their final state, do not comply. These cements initially withstand cycling, but subsequently develop leaks; they include the more flexible surface-catalysed compositions mentioned in the earlier report (E.R.D.E. TR.2/63). Ten cements, having moduli ranging from 300 p.s.i. (rubber) to 400,000 p.s.i. (rigid plastic), do not comply, and all these leak on thermal cycling. Thus the experimental results confirm the requirements. The equation given will permit the calculation of the effect on sealing of temperature changes on cemented threaded joints of any materials, whatever their dimensions. The paper has been accepted for publication by "Engineering Materials and Design".

Of the six cements which resist thermal cycling, only two are likely to be generally useful to the Services, and arrangements have been made with the manufacturers for the supply of sufficient material for storage trials.

#### Temporary Seals for Aircraft Fuel Tanks

UNCLASSIFIED

Six fuel-resistant lutings, having a range of yield values, are now ready for a trial to be arranged in the near future by the Fire Service.

#### Adhesives Strength of Lap Joints:

E.M.R. with Royal College of Science and Technology

UNCLASSIFIED

As stated in the last progress report E.R.D.E. TR.2/63 it was proposed to examine the correlation, if any, between the breaking load for an actual lap joint and the bending moment factor as specified by Goland and Reissner (1944) and illustrated photoelastically by

/McClaren .....



McClaren (1961). Due to practical difficulties in making and testing joints in the college very few results have been obtained.

This correlation is now being examined at E.R.D.E. Test pieces, assembly jigs and testing equipment have been designed and made. Joints have been made between very carefully prepared cast steel adherends in which the glue line thickness can be controlled to within  $\pm 10$  per cent. A load can be applied to these joints in such a way that the previously mentioned bending moment factor can be varied from  $+2/3$  to  $-2$ . Initial experiments have been completed but it is not possible yet to draw any conclusions from the results.

Rubber-Proofed Fabrics

UNCLASSIFIED

The investigation into the effect of temperature and aromatic fuel on the endurance of cemented joints between proofed fabrics is continuing.

Routine investigation of adhesion of proofing to fabric and permeability of proofed fabric to fuel have been carried out from time to time.

A Non-Destructive Test for Glued Joints

UNCLASSIFIED

W. Thompson of A.I.D. has reported a non-destructive method of testing glued joints between light alloy adherends (A.I.D. Report NDT/1785). He assumes that the strength of the joint is related to the compressive stress imposed on the adherend by the adhesive due to the latter's change in volume during cure. The compressive stress he relates to the resistance offered by one adherend to thermal expansion. By measuring the time taken for the adherend to extend a fixed distance, the author was able to forecast the strength of the joint when tested in shear.

A similar apparatus has been built in E.R.D.E. and attempts are being made to obtain reproducible results.

Adhesion of Proofing to Fabric:

E.M.R. at the National College of Rubber Technology

UNCLASSIFIED

Initial experiments on the role played by isocyanates in the bond between nitrile rubber and nylon have been made. When nylon film has been exposed to isocyanates in boiling toluene there is evidence of chemical attack and infra-red spectrographs support the presence of a chemical bond between the nylon and the isocyanate.

Adhesion of Surface Coatings

Tests on Coated Panels

UNCLASSIFIED

A technique described by the Joint Services Committee on Paints and Varnishes (Journal of the Oil and Colour Chemists Association 1963, 46, 276) has been used to determine the adhesion of surface coatings during exposure trials. Discs are cut from the exposed panels after various periods of exposure and bonded between standard adhesion

/test-pieces .....



test-pieces, using an epoxide adhesive. After curing at room temperature for a week, the assembly is loaded in direct tension and the failing load recorded. Usually, the coating either is detached completely from the substrate (adhesion failure) or fails cohesively in the coating.

This method has been used to study changes in the adhesion of phenolformaldehyde lacquer (to specification C.S.2465B) applied to mild steel panels and cured at various temperatures before exposure outdoors. Unexposed films (controls) stoved below 100°C failed in adhesion under tensile stress of about 800 g/mm<sup>2</sup>. Controls stoved above 100°C failed cohesively at about 2500 g/mm<sup>2</sup>. During 2 months outdoor exposure failing stresses increased by 12 - 25 per cent, and films stoved below 100°C failed cohesively close to the metal substrate. Films stoved above 100°C failed cohesively, in the same way as the controls.

Six surface-coating systems (i.e. primer, undercoat and top coat(s)) are being exposed out of doors at E.R.D.E. and at J.T.R.U. Australia, and physical properties and adhesion are being compared during the early stages of exposure (after 10, 100 and 250 days). Adhesion measurements to date indicate good agreement in the character of failure although, as expected, the changes in bond strength at the two places are different.

One objection to the above method of test is that the epoxide adhesive used requires up to a week at room temperature to develop sufficient strength to remove many coatings, and, during this period, changes in adhesion may occur.

Recent collaborative work with the Joint Services Sub-committee on Adhesion and Accelerated Weathering of Paints suggests that the adhesion of many surface coatings may be determined within an hour of removal from exposure by using a rapid setting cyano-acrylate adhesive (Eastman 910).

#### Effect on Adhesion of Immersion in Sea Water

UNCLASSIFIED

Using Eastman 910, changes in adhesion which occur after removal from sea-water have been examined. The coatings tested were two oil-modified alkyl paint systems, consisting of primer, undercoat and two top coats on mild steel panels, before and after immersion in sea-water for one week. Both paint systems gave very similar results at every stage, and these may be summarised as follows:

- (a) before immersion (controls), the systems had a bond strength of about 1300 g/mm<sup>2</sup>, and showed some adhesive failure between the two top coats, together with various cohesive and adhesive failures in other coats, except the primer. No failures in adhesion between the primer and metal occurred.
- (b) one hour after removal from sea-water, the bond strength was only about 25 per cent of the control, and the failures were in adhesion between the metal and primer, and between the primer and undercoat.
- (c) 24 hours after removal, the bond strength was only slightly lower than that of the control, but the mode of failure remained similar to (b) above.

/(d) .....



- (d) 150 hours after removal, the bond strength was similar to the control, but the mode of failure was again similar to (b).

### 7.3 CERAMICS AND REFRACTORIES

#### Fibres - $\text{Si}_3\text{N}_4$ Whiskers

UNCLASSIFIED

Considerable effort is being put into the design of the larger-scale  $\text{Si}_3\text{N}_4$  furnaces (Bran-tub II). These have each about ten times the capacity of the present semi-scale furnace (Bran-tub I). Since the cost and delay in building such a plant is largely in the ancilliary equipment and the cost of the actual reaction vessel or tub is modest (about £500) these tubs are being duplicated so that production can be switched to the second tub while the first is cooling and being recharged. In this way most of the advantages of continuous production should be realised. It would be advantageous in Bran-tub II to change from carbon wool insulation to refractory bricks. Current experiments with Bran-tub I indicate that brick insulation works, but with a reduced yield, and the reasons for this are being investigated.

#### SiC Whiskers

UNCLASSIFIED

It is necessary to use chemical rather than physical processes for making refractory whiskers because this is the only way in which they can be grown at a reasonable temperature (about  $1500^\circ\text{C}$  instead of say about  $2500^\circ\text{C}$ ). Unfortunately it seems that such reactions can only yield useful whiskers when the free energy change is quite small. Since at the reaction temperature, ten or a dozen vapour species may be present it is impracticable to achieve growing conditions by an experimental approach and it is necessary to make use of computer techniques since the energy balance is very complex. It seems that  $\text{Si}_3\text{N}_4$  is reasonably tolerant (which is perhaps why we have been able to grow  $\text{Si}_3\text{N}_4$  whiskers) but that the conditions for the more desirable SiC whiskers must be computed. This is being done and it is hoped to realise conditions for both whisker and film growth of SiC. Although the programme is still awaiting time on Mercury, preliminary estimates show that besides Si, C, O and H, a halogen (probably  $\text{Cl}_2$ ) will have to be introduced into the system. This is relevant to the N.G.T.E. E.M.R. at Leeds University.

#### $\text{Al}_2\text{O}_3$ Whiskers

UNCLASSIFIED

In view of the interest expressed at Aldermaston and elsewhere, we have made a few further experiments in a tube furnace in growing  $\text{Al}_2\text{O}_3$  whiskers. These experiments were made using the wet hydrogen process and double walled tubes, the degree of experimental control being greater than is usually the case elsewhere. Yields are small and generally of poor quality and this has confirmed our view that  $\text{Al}_2\text{O}_3$  can only be grown by relying on computer and mass-spectrographic techniques, especially since two volatile species of aluminium oxide exist and  $\text{Al}_2\text{O}_3$  has 13 polymorphs. There are also many other complications. We think that given a sophisticated approach success

/could .....



could be achieved, if it were worth the effort, but it will be recalled that several American Laboratories have been working on the process for about five years, so far as is known without success.

Continuous Fibres

UNCLASSIFIED

We are taking an interest in the production of continuous high-stiffness fibres both by carbon-conversion and by Taylor wire methods. The latter seems to offer the best prospect of making effective use of beryllium and boron.

Preparation of Experimental Two-phase Materials

UNCLASSIFIED

Whatever reinforcing fibre is used it must be packed efficiently into the material and this usually necessitates orienting the fibres parallel to each other; the best volume packing which can be got from non-parallel arrangements is about 30 per cent. With continuous fibres, parallel packing is simple but using short and small fibres such as whiskers the difficulties are considerable. Two parallelising techniques are being developed. In the first, a slurry of whiskers in a liquid of controlled viscosity and surface tension is passed under a vibrating grooved bar. This process is promising and may have wider applications but the conditions are critical and development will take a little time. In the second process whiskers are suspended in an aqueous solution of ammonium alginate and are extruded through a nozzle into a bath of dilute hydrochloric acid.

The alginate is coagulated and the whiskers "frozen" in the parallel position as they emerge from the die. The resulting thread is dried and the alginate burnt off resulting in an almost truly parallel arrangement of whiskers. At the time of writing, packing factors up to about 55 per cent have been achieved.

Whiskers/Resin Systems

UNCLASSIFIED

In the earlier work shear-lag in the resin was a drawback. This is being countered by better packing (see above) and by the use of stiffer resins. Large improvements await the progress of the orientation experiments.

Whiskers/Metal Systems

Silver/Si<sub>3</sub>N<sub>4</sub> System

UNCLASSIFIED

Small additions of silicon have given improved properties in composites at high temperatures, apparently by improved adhesion. At small volume fractions of whiskers (about 6 per cent) a curious weakening of the matrix occurs, which in turn implies that the degree of reinforcement attained with somewhat larger volume fractions was greater than first thought. This effect is being investigated. There is no observed dispersion hardening effect of whiskers in silver with the result that the useful elastic range is minute. Attempts will be made to examine the mechanical behaviour of a more elastic alloy, since irrecoverable plastic strains have been measured at strains involving the efficient utilisation of whiskers.

/Preliminary .....



Preliminary experiments with alloying additions of palladium powder to the silver-whisker materials have yielded higher melting alloys in which whisker strength appears to be retained at temperatures of about 1000°C. On aging at 1100°C, however, there is observable attack on the whiskers but much less serious than has been observed in other high melting metals. It is possible that further examination of different alloy compositions and/or protective coating of the whiskers could yield a directly useful material.

Compatibility Studies

UNCLASSIFIED

In addition to the above Pd/Ag alloy, alloys of nickel with aluminium and chromium have been investigated for their stability with  $\text{Si}_3\text{N}_4$ . Both of these additions lead to rapid recrystallisation of  $\text{Si}_3\text{N}_4$  with little or no direct chemical action. A similar effect was found with cobalt yet no effect was found with prolonged heating of  $\text{Si}_3\text{N}_4$  in a molten Ag-Si alloy. The mechanism of this process is not understood, but the observations have much in common with the tendency of thermodynamically stable dispersions to agglomerate in the above matrices, which is found in orthodox metallurgy.

7.4 ELECTRONIC MATERIALS

UNCLASSIFIED

Much of the theoretical aspect of this research is closely allied to the computational work which is going on under 7.3 above and will not be described separately. Experimental work, apart from the construction of furnaces of more advanced design, has mostly been directed to the preparation of mixed crystals of gallium arsenide and gallium phosphide, so far without success.

7.5 TROPICAL RESEARCH AND TESTING

Joint Tropical Research Unit, Queensland, Australia

UNCLASSIFIED

From measurements made in the first year on rates of degradation of steel panels and of polythene sheet, it has been shown that the effects of outdoor exposure at the hot-wet site at Innisfail and at the hot-dry site at Cloncurry are of the same order as those obtained on the corresponding sites at Port Harcourt and Kano, Nigeria, operated until recently by the M.O.S. Tropical Testing Establishment.

The number of exposure trials, of both U.K. and Australian origin, continues to grow. They cover in the main the study of degradation in light alloys, paints and polymers, including polyolfines, glass-fibre laminates, polycarbonate, polyacetal, and a range of rubbers and related elastomers.

A marine site is being developed for exposure to tropical seawater.

/Work .....



Work continues on the temperatures reached in structures exposed to intense solar radiation with diurnal variation. First results on surface temperatures confirm those obtained in other similar trials, and the work is being extended to include temperature contours within composite bodies.

Tropical Exposure of Rubbers

UNCLASSIFIED

Vulcanizates of various elastomers, namely, natural rubber, nitrile rubber, neoprene WRT, neoprene ILA, PVC/nitrile-rubber blend, ethylene/propylene terpolymer, a fluorinated copolymer, polyester-urethane and polyether-urethane are being prepared for exposure on three sites at the Joint Tropical Research Unit in Australia. The aim is to compare the rates of degradation of these elastomers and to seek correlation with those rates obtained from certain laboratory tests.

Tropical Exposure of Plastics

UNCLASSIFIED

Laboratory tests have been shown that polyacetals will degrade when exposed to 100 per cent relative humidity at 70°C.

Two grades of the homopolymer (natural and black) and two similar grades of the copolymer are being moulded into test-pieces for exposure in three sites (hot-dry; hot-wet, clearing; and hot-wet, jungle). The rates of degradation of the four grades will be compared with those tested under laboratory-controlled environments.

It was found that a chlorinated polyether was practically unaffected by accelerated aging tests in the laboratory. This material is also being prepared for exposure and comparison with laboratory tests.

/8 .....

8.1 UNIT OPERATIONSCrystallisation

UNCLASSIFIED

A more refined apparatus, based on the dipping refractometer principle applied in earlier work, has been set up for measurement of growth rate, and a programme has been started which will yield growth rate data and provide experience on the reliability of the apparatus. Sodium thiosulphate pentahydrate crystals 300 - 400 microns in diameter at 25°C gave a growth rate of 10 microns/minute per 1 per cent supersaturation, and unlike other materials so far measured, its growth rate did not increase with larger crystal size. This has not been explained. Further growth-rate measurements on ammonium perchlorate were made, but disclosed anomalous solubility figures quoted in the literature, which show discrepancies of 7 per cent and invalidate supersaturation values. New solubility determinations have therefore been made and indicate that the figures quoted by Seidel in "The Solubility of Inorganic and Organic Compounds" are correct.

Information on ammonium perchlorate growth rates is needed for studying the performance of the Kestner evaporative crystalliser. In some preliminary work, the effect of variations in the feed rate, feed concentration, and operating vacuum on the crystal size has been determined. In general, increases in throughput or operating temperature lower the average crystal size.

Experiments are now being made observing crystallisation in stirred vessels where the rate of cooling is accurately controlled by the electronic cooling controller described in the last report (pp. 53 and 55). Ammonium perchlorate/water is the system mainly employed. The rate of cooling seems to affect the nucleation phenomena considerably both before and after reaching saturation point, and a reproducible concentration change (measured by refractive index) has been detected even before the first nucleation can be detected visually. A literature survey is being made on aspects of agitation relevant to crystallisation from stirred solutions, including scale-up aspects.

Experience in producing spheroidised ammonium perchlorate was described in the last report. The extension of this work to RDX has been accomplished by carrying out the operation in cyclohexanone instead of water. This confirms that an important feature in spheroidising is the dissolving and recrystallising of fines formed by the grinding action. Pilot plants have been set up for processing on the 2 to 10 lb. scale, and a range of spheroidised RDX has been made from 50 to 500 micron average size.

/8.2 .....



## 8.2 EQUIPMENT STUDIES

### Propellant Mixers

UNCLASSIFIED

A method has been developed (described previously) of monitoring the clearances between the agitator blades and walls in mixers, which depends on measuring the capacitance of such a gap. This is suitable for inspecting assembled empty mixers, but is unlikely to be so for mixers in operation because of the varying dielectric constant of the medium (propellant, air, vacuum etc.) in the gap. The principle most likely to be useful is magnetic induction because the magnetic permeabilities of the media in the gaps and of the non-magnetic metals used for explosives mixers are all very similar and close to unity. Experiments are in hand in which a permanent magnet is embedded in the tip of an agitator blade and the voltages induced in search coils placed outside the vessel (and jacket) walls are recorded as the agitator rotates. The possible variables in the system e.g. strength of magnetic field, inductance of pick-up coils, distance between magnet and coil, speed of rotation, drift of associated electronic equipment and the effect of interference have been studied in laboratory set-ups. Results indicate that the method should be feasible on an actual mixer, provided there is not excess interference, with an accuracy of  $\pm 1/32$  inch on a clearance of  $\frac{1}{4}$  to  $\frac{3}{8}$  inch with a 2-inch gap between magnet and coil.

### Noise Hazard from Explosion Cupboards

UNCLASSIFIED

In designing an installation of explosion cupboards in new laboratories it was desired to protect the operator and other personnel in the laboratory from noise in the event of an explosion in a cupboard, as well as from blast and fragments, against which existing designs give protection. If a cupboard is placed behind a screen, the construction of the screen must be such as to attenuate and not amplify noise.

Trials are planned to compare noise in a mock-up room resulting from explosions in a cupboard with different designs of screen. Since no method was known of obtaining any single measurement of the acoustic effects of explosion, suitable tape recording equipment was designed and obtained so that noise could be recorded and examined subsequently. Several detonations of 10-gram tetryl pellets have been recorded under different dispositions to determine the effect of confinement, attenuation by a brick wall, reverberation by steel plates and whether the noise is attenuated by closed cupboard doors. Preliminary results indicate that a steel screen acts as a diaphragm and is of no value in attenuating the noise. Experiments on damping will be performed on the steel sheets, but it appears that material of high mass and low elasticity such as brick or loose packed sand is preferable for a screen wall.

### Instrumentation Systems

UNCLASSIFIED

Acoustic measurements are being made in the investigation described above on noise from explosion cupboards. A calibrated amplifier has been designed and made to provide a measurement range of + 60 db to + 160 db in switched 2 db steps (standard reference pressure 0 db = 0.0002 dynes/sq.cm). The unit accepts signals direct from a

/specially .....



specially calibrated microphone and feeds standardised output signals to the associated tape recorder and to a peak voltmeter used for setting and monitoring peak recording level. Another amplifier is included in the unit, incorporating another attenuation ganged to the first, to provide a controllable low impedance output from the tape recorder replay signal. Performance of the system is such that bandwidth is limited only by the microphone characteristics, and signal-noise ratio limited by recorder noise. Overall calibration accuracy is within  $\pm 2$  db. A high quality amplifier and loudspeaker are being used to permit subjective comparisons being made of different recorded effects. It is hoped that a measurement method will be found to provide reasonable correlation between subjective assessments and a single measured quantity.

A pressure measuring system has been designed in connection with the development of initiators operating at elevated temperatures. The initiators, which are fired electrically, produce pressures approaching 3,000 p.s.i. and rise times varying between 0.2 to 5.0 milliseconds in a chamber volume of 0.05 cu.inch. The pressure vessel is designed to accept a standard capacitance gauge. This type of gauge has a rugged construction and can withstand the heavy overloads which may occur. Gauge output is in the form of capacity varying linearly with pressure and this is applied to a recording system which converts the capacitance variation into a voltage variation to drive a cathode-ray tube in the "Y" direction. A drum camera records the pressure-time curve and controls the firing, thus ensuring correct event positioning on the photographic record. The firing chamber has now been re-designed to minimise the time taken in assembly and dismantling.

Investigation into the fluoroscopic properties of materials required the use of a high-pressure Xenon discharge lamp producing intense radiation from 2,000 to 10,000 Å. A power supply has been designed to provide a 30 kilovolt ionisation pulse and a 100 volt d.c. output with a ripple content less than 1 per cent peak to peak to operate the lamp. When the lamp strikes, its terminal voltage reduces to 22 volt and the current is limited to 25 A by a series resistor which is forced-air cooled. Stability of lamp intensity is increased by operating the supply from a single-phase a.c. stabiliser. To obtain extra stability a provisional system has been designed in which the lamp current will be controlled by a signal derived from the light output.

To assist in the study of the expansion of polymers with respect to temperature a system has been developed incorporating commercial instruments. A two-channel potentiometric recorder plots the temperature and expansion continuously during an eight hour period. The temperature is measured by thermocouples over the range  $-75^{\circ}\text{C}$  to  $+225^{\circ}\text{C}$  in ten ranges, employing an ice-point reference. A backing-off potential is provided to allow the recorder zero to be set so that the experiment may be started at any pre-determined temperature. The expansion, which is in the range 0 - 0.001 inch is measured by a displacement transducer whose output is converted to produce a voltage acceptable to the recorder. To avoid overloading the recorder a safety circuit is provided to switch off the apparatus when full scale deflection occurs.

/2 .....



2 CHEMICAL ANALYSIS (INCLUDING PHYSICAL METHODS)

9.1 CHROMATOGRAPHY

Thin-Layer Chromatography

UNCLASSIFIED

The quantitative method for the determination of diphenylamine (DPA) by thin-layer chromatography has been modified. In order to locate the exact position of the DPA, the chromatoplate is sprayed with an alcoholic solution of dichlorofluorescein, and viewed under ultra-violet light. DPA shows up as a dark purple zone on a light purple background.

Several different thin-layer chromatographic techniques have been examined. These include the use of the Stahl chamber, horizontal development, two dimensional development, continuous elution, and multiple unidimensional chromatography. The last three methods have been applied specifically to the separation of a mixture of diphenylamine derivatives.

9.2 SPECTROSCOPY

Nuclear Magnetic Resonance Spectroscopy

UNCLASSIFIED

A Perkin Elmer R.10 spectrometer has been installed with facilities for measuring hydrogen, fluorine and boron resonance spectra. Routine spectra can now be measured for structure determination. An investigation has commenced on the effects of solvents on hydrogen spectra.

Infra-red Spectroscopy

UNCLASSIFIED

Rotational isomerism in nitric esters of the general formula  $\text{CH}_2\text{X}.\text{CH}_2\text{ONO}_2$  where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ,  $\text{ONO}_2$  is being studied by infra-red spectroscopy. Results so far indicate that only the chloro and bromo compounds can exist in both trans and gauche forms.

9.3 CRYSTALLOGRAPHY

Aluminium Hydride

CONFIDENTIAL/DISCREET

In order to determine the positions of the hydrogen atoms, the integrated intensities of the X-ray reflexions have been determined as accurately as the available equipment would allow. Errors in intensity measurements may arise from specimen absorption, extinction, and particle size effects. To these may be added instrumental factors such as dead-time and waveform corrections for the Geiger counters which had to be used, the presence of harmonic and other unwanted wavelengths in the X-radiation and variable absorption by the air path of the X-rays, due to changes of temperature and pressure.

/Attention .....

Attention has been given to correcting the measured X-ray intensities for these sources of error and the first set of measurements has been used in structure calculations; a second set of intensity measurements, using a new specimen, is nearly complete and will provide information on the influence of specimen particle size effects and on how far refinement of the results is justified.

The observed intensities were corrected for Lorentz-polarization factors and multiplicity, and the derived structure factors were used in estimating anisotropic thermal vibration factors for the aluminium atoms, and the scale factor. A set of calculations was then carried out for the aluminium part of the structure to compare the calculated and observed structure factors; thermal parameter B parallel to the c-axis was taken as 1.18, and perpendicular to the c-axis it was taken as 0.76.

The residual  $R (= \sum |F_{\text{obs.}} - F_{\text{calc.}}| / \sum F_{\text{obs.}})$  is not entirely suitable for use in the discussion of results for a structure of the present kind, but it was found that the value obtained did reflect the quality of agreement between the calculated and observed results, and is quoted here. For the aluminium atoms,  $R = 0.046$ .

The effect of including hydrogen atoms was next considered. Assuming space-group  $R\bar{3}m$ , the hydrogen atoms can be in positions  $\frac{1}{2}00$  etc. or  $\frac{1}{2}0\frac{1}{2}$  etc. (hexagonal axes). Calculations using the first set of positions did not greatly change  $R (= 0.050)$  but the pattern of agreement was adversely affected. Using the second set of positions,  $R = 0.028$ , and the pattern of agreement was improved. An estimated correction of the intensity data for extinction effects further improved  $R$  to 0.022.

The set of positions at  $\frac{1}{2}0\frac{1}{2}$  etc. places each hydrogen atom mid-way between two aluminium atoms situated at corners of the rhombohedral cell; the distance between these aluminium atoms is 3.240 Å, and so the Al-H separation is 1.620 Å. The structure may be envisaged as a slightly distorted simple cubic array of aluminium atoms with hydrogen atoms situated midway on the cube edges; the distortion is an extension of about 5 per cent along one cube diagonal. The hydrogen atoms adjacent to any one aluminium atom are in an octahedral arrangement which is slightly distorted.

#### Nitramine Chemistry

UNCLASSIFIED

The compound suspected to be 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane has been examined by X-ray methods.

The following crystal data were determined:

/Space-group .....



Space-group:	P2 <sub>1</sub> /a
Unit cell parameters:	a = 11.79 A
	b = 14.56
	c = 7.54
	= 140° 33'
Density:	1.444

This space-group accommodates two centrosymmetrical units, or four units in which symmetry is not necessarily implied. In the latter case the calculated molecular weight is  $231 \pm 3$ , in reasonable agreement with the value of 235 required by the supposed formula.

(In E.R.D.E. TR.2/63, p. 58, line 11 from bottom of page, the symbol should be  $\alpha$ , not  $\theta$ .)

#### 9.4 RADIOCHEMISTRY

##### Molecular Weights of Polymers

UNCLASSIFIED

Experiments have been started to develop a radiochemical method for determining the number-average molecular weight of polymers which have labile hydrogen end-groups, e.g. -OH, -NH<sub>2</sub>, -COOH ended polymers. Polystyrene mixed with small quantities of cetyl alcohol has been chosen as the model system. Attempts are being made to utilise an exchange reaction between the hydroxyl hydrogens and tritium using tritiated water dissolved in benzene-tetrahydrofuran mixtures. In principle the method is capable of determining molecular weights greater than 10<sup>6</sup>, but it is possible that the presence of adsorbed water molecules on the polymer will greatly reduce this sensitivity. In order to minimise this, the experiments are being conducted under high vacuum using freeze-drying techniques.

##### Thermal Degradation of Polymers

UNCLASSIFIED

Work on the degradation of polystyrene-poly( $\alpha$ -methyl styrene) mixtures has been continued and a quantitative assessment made of the nature of the processes involved.

Experiments which studied the effect of the concentrations of the two components can best be explained by assuming the system to be inhomogeneous and to consist of micelles of poly( $\alpha$ -methyl styrene) in a matrix of polystyrene. Macroscopic examinations of a large number of casts of these mixtures have not revealed any inhomogeneities, but the sensitivity of this method is largely governed by the difference in the refractive indices of the components which in this case is probably very small. A recently published paper, however, in which mechanical and physical properties of these mixtures were described, also suggests the system is inhomogeneous.

/Experiments .....

Experiments to determine the effect of poly( $\alpha$ -methyl styrene) molecular weight on the degradation pattern of these mixtures have been carried out over a temperature range of 260° - 286° C. Results show that the rate constant for scission of the inter-unit bond in poly( $\alpha$ -methyl styrene) can be described by the equation:

$$k_i = 5 \times 10^{18} e^{-63000/RT}$$

This result is in good agreement with published work on the degradation of pure poly( $\alpha$ -methyl styrene).

Analysis of the styrene given off in these experiments indicates that the polystyrene is only initiated by the  $\alpha$ -methyl styrene radical monomer which is produced by complete unzipping of the poly( $\alpha$ -methyl styrene) chain. This is explained by the assumption that only the monomer radical can diffuse out of the micelles and into the polystyrene matrix. Using this model it is possible to estimate that the activation energy of depropagation of polystyryl radicals = 21.5 kcal/mole and that:

$$\frac{k_d}{\sqrt{k_t}} = 3 \times 10^2 e^{-11500/RT}$$

where  $k_d$  = rate constant of depropagation of the polystyryl radical

and  $k_t$  = rate constant of termination of the polystyryl radical.

/List .....



List of Reports Bearing the Grading "Discreet"  
Issued by E.R.D.E. in the Period 1.1.64 to 30.6.64

Classification Key: S/D = SECRET/DISCREET  
C/D = CONFIDENTIAL/DISCREET

Number	Classi- fication	Author	Title
13/R/63	C/D	A. Davis, J. Powling and M.J.L. Sheppard	Factors Influencing the Utilisation of Aluminium in E.R.D.E. Propellants
14/M/63	C/D	J.A. Bell and I. Dunstan	Preparation and Characterisation of Di(B-cyanoethyl)2,3- dihydroxypropylamine
TR.2/63	S/D		Technical Report for the Period 1.7.1963 to 31.12.1963

/List .....

List of Reports and Technical Memoranda  
Issued in the Period 1.1.64 to 30.6.64

Classification Key: C = CONFIDENTIAL  
R = RESTRICTED  
U = UNCLASSIFIED

Number	Classi- fication	Author	Title
11/R/63	C	L.E. Grindrod, D.L. Hodge and R. Tinniswood	Calorimetry of High-Energy Rocket Propellants Containing Ammonium Perchlorate and Aluminium
12/R/63	C	N.J. Blay and (Mrs.) P.E. Fuller	The Titrimetric Estimation of the Hydroxyl Content of Polyesters and Polyglycols, Using Acid Catalysed Acetylation Reagents
16/R/63	U	D. Sims	Polymerisation of Tetrahydrofuran: Part I
17/R/63	R	J.A. Bell and I. Dunstan	The Chemistry of Nitramines: Part II. Preparation and Reactions of the Condensation Products of Ethylenedinitramine with Formaldehyde and some Diamines
18/R/63	U	R.W. Gooding	The Manufacture of Refractory Oxides and Nitrides by the Method of Reaction Sintering
20/R/63	U	G.J. Spickernell and J.H.C. Vernon	The Age-Hardening of Plastic Propellant
24/R/63	U	R.R. Fergusson and T. Gabor	The Transport of Gallium Arsenide in the Vapour Phase by Chemical Reaction
25/R/63	U	D.H. Richards	The Behaviour of Stannic Acid Sols in Concentrated Hydrogen Peroxide: Part IV: Quantitative Evaluation of the Precipitating Efficiency of Aluminium ions

/List (continued) .....



List of Reports and Technical Memoranda  
Issued in the Period 1.1.64 to 30.6.64 (continued)

Number	Classi- fication	Author	Title
4/M/63	C	R.S. Smith and G.W. Stocks	A Study and Tentative Explanation of Two Phenomena Related to the Erosion of Graphite Expansion Nozzles
8/M/63	U	D.A.G. Eldridge and A.D. Short	A Four-Channel Automatic Recording System for Propellant Evaluation
9/M/63	R	B.G. Barnard and E.T. Brett	Assessment of a Commercial Xeroradiographic Equipment for the Inspection of Rocket Propellant Charges
10/M/63	U	R.W. Bryant, W.A. Dukes and (Mrs.) J.V. Long	Commercial Lutings
11/M/63	C	R.W. Rainbird and J.H.C. Vernon	The Rheology of Case-Bondable Cast Double-Base Propellants: E.R.D.E. and I.C.I. Studies on the Effects of Alternative Plasticisers
13/M/63	R	M.J.L. Sheppard, R.S. Smith and G.W. Stocks	Measurements of Heat Loss in Thick-walled K-round Motors
17/M/63	U	A.W. Feraday, R.F. Long and J.H.C. Vernon	The Strain Distribution in a Biaxially Stretched Diaphragm of Solid Propellant

/Papers .....

~~SECRET/NOFORN~~  
UNCLASSIFIED

Papers Published in the Open Literature  
in the Period 1.1.64 to 30.6.64

Authors	Title	Journal Reference	File No.
L.J. Bellamy, A.R. Osborn and R.J. Pace	Infra-red Studies of the Deuterium Isotope Effect in Acids	J. Chem. Soc., 1963, 3749	WAC/ 142/044
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